SOME NITROSONIUM AND NITRONIUM SALTS OF STRONG ACIDS

THESIS

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by

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C O N T E N T S

A B S T R A C T

A series of compounds, reported in the literature, which can be formulated as nitrosonium salts of fluoro-acids, have been re-prepared. Several metal chloride-nitrosyl chloride adducts, also reported in the literature, have been re-prepared, and both these groups of compounds have been shown to contain the nitrosonium ion, NO^+, by infrared diagnostic methods.

The isomorphism of the nitrosonium salts of the anions fluoroborate, chlorostannate and chloroplatinate with their potassium analogues has been confirmed, and nitrosonium and potassium fluorosulphates have been shown to be isostructural. These observations have been explained structurally, with reference to the relative sizes of nitrosonium and halide ions.

The free (i.e. unco-ordinated) nitrosonium ion was found to absorb in the region 2160 cm^{-1} - 2400 cm^{-1}. This wide variation was partially explicable in terms of polarisation by the anion but it is apparent that other factors were important. In general, it was found that fluoro-acid salts gave the highest nitrosonium ion stretching frequencies, followed by oxy-acid salts and chloro-acid salts respectively.

The behaviour of group IVB and VB Lewis acid halides was observed with nitrogen oxides and nitrosyl chloride. With dinitrogen tetroxide, all the compounds examined, except arsenic trichloride, gave a mixture of products which it was not possible to separate. Arsenic trichloride gave a nitrosonium nitrato-arsenate salt. In the other cases, there was evidence for the formation of nitrosonium and nitronium salt mixtures, in accord with earlier observations on the behaviour of dinitrogen tetroxide with Lewis acids, and strong acids such as perchloric acid. With nitrosyl chloride, the products were either nitrosonium chloro-acid salts or molecular adducts. Reactions involving nitric oxide were not investigated extensively but in reactions with high valency metal chlorides, the primary reaction step was always a reduction by the nitric oxide.

The behaviour of transition metal chlorides and oxides of the titanium, vanadium and chromium groups was observed in nitrosyl chloride and dinitrogen tetroxide. These reactions could all be explained assuming auto-ionisation of the solvent.

The reactions in nitrosyl chloride yielded mainly nitrosonium salts of chloro-acids, and several of the anions thus formed were bi- and tri- nuclear species.

The previously reported compounds $NO.VCl_4$ and $NO.V_2Cl_7$ were obtained and characterised as nitrosonium salts. With niobium and tantalum, the new compounds $NO.NbCl_6$ and $NO.TaCl_6$ were prepared, containing the previously unknown $NbCl_6^-$ and $TaCl_6^-$ anions. The new compounds $(NO)_3\ Cr_2\ Cl_9$ and $(NO)_3\ Mo_3\ Cl_{10}$ were obtained. A surprising feature of several of these ionic compounds was their high volatility.

In the reaction between chromium (VI) trioxide and nitrosyl chloride, a new compound $(NO)_2\ Cr_3\ O_8\ Cl$ was characterised, in which chromium has undergone a partial reduction. Vanadium pentoxide underwent a similar reaction, but in this case it was not reproducible.

The reactions involving dinitrogen tetroxide with transition metal ha generally gave rise to one product only, in contrast to the Lewis acid - dinitrogen tetroxide reactions. The products were usually metal nitrate-dinitrogen tetroxide adducts and these could be formulated as nitrosonium metal nitrato-salts, on the basis of their infrared spectra. Vanadium and chromium chlorides gave the adducts $VO_2NO_3.N_2O_4$ and $Cr(NO_3)_3.2N_2O_4$ respectively, but molybdenum trichloride gave $Mo(V)O(NO_3)_3$, which may be polymeric.

No reaction occurred between chromium (III) chloride and either nitrosyl chloride or dinitrogen tetroxide, but in the presence of chromous chloride, reaction proceeded

readily in both instances.

No reaction was observed between high valency metal oxides and dinitrogen tetroxide, but this may have been due to insufficiently vigorous conditions.

The reflectance spectra of the majority of the above compounds were observed, and, in most cases it was possible to make satisfactory band assignments.

ACKNOWLEDGMENTS.

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INTRODUCTION

Much of the early work on systems involving nitric oxide complexes stemmed from observations on two important reactions, one in the industrial context, the other in analysis:

1. The lead chamber process for the commercial production of sulphuric acid was known to proceed via a blue crystalline intermediate, the familiar 'chamber crystals'; this substance was known to be an essential step to the eventual formation of sulphuric acid, and from it a yellow hygroscopic crystalline solid was obtained, $NO.HSO_4$, nitrosyl hydrogen sulphate, whose structure aroused considerable interest. The outstanding pioneer in this field was Hantzsch, who, between 1905 and 1930, published a series of papers on the behaviour of nitrosyl hydrogen sulphate in solutions of strong acids, and later extended this to nitric acid/strong acid systems. His work and conclusions were largely concerned with cryoscopic and electrolytic observations, and he was the first person to postulate the existence of the nitrosonium ion NO^+.

2. The 'brown ring' test for nitrate ion, involving formation of an unstable complex of ferrous sulphate, has been familiar for many years but only recently has the

constitution of this complex been unambiguously assigned. Manchot was prominent among the early workers in this field, and he observed that the 'brown ring' complex was identical to that formed when ferrous sulphate solution absorbed nitric oxide. Manchot and his co-workers were able to establish the metal: nitric oxide mole ratio in the complex, and in 1924, electrolytic experiments confirmed that the nitric oxide was associated with the metal. In addition, nitric oxide complexes of cupric and palladium salts were studied; from the former, by comparison with cuprous/carbon monoxide systems, a relationship was noted between nitric oxide and carbon monoxide complexes, which was later amplified by Hieber and Anderson.

Both these areas of research began in the early twentieth century. In the nineteen twenty's another significant field appeared when Gall & Mengdehl, and Rheinboldt & Wasserfuhr, simultaneously reported the formation of adducts between nitrosyl chloride and various metal and non-metal chlorides. These complexes, like nitrosyl hydrogen sulphate, were hygroscopic solids; they were susceptible to x-ray examination, and by these means Klinkenberg, in 1937, confirmed the existence of the nitrosonium ion in some of the adducts. Magnetic

susceptibility determinations were carried out by Asmussen in 1939 but, structurally, these were much less conclusive. Meanwhile, Angus & Leckie, in 1935, had laid the basis for possibly the most powerful diagnostic tools in this field, Raman and infra-red spectroscopy. By observations on the Raman spectrum of nitrosyl hydrogen sulphate in sulphuric acid/water solutions of varying concentrations, they were able to assign a Raman band to the nitrosonium ion.

After the war, studies were extended to nitrosonium and nitronium metal fluorides, and to metal nitrate: dinitrogen tetroxide complexes, which are analogous to the metal chloride: nitrosyl chloride adducts in some respects; this will be enlarged upon in a later chapter. Addison and his school have published a number of papers on the dinitrogen tetroxide solvent system, and more recently, this has been extended to studies on anhydrous transition metal nitrates, which were, until recently, unknown.

Raman and infrared spectroscopy have been developed much more than the other diagnostic methods. Ingold and his co-workers extended this to cover systems containing nitronium, NO_2^+, ions, and Griffith, Lewis & Wilkinson extended infrared spectroscopy to other nitric oxide - metal complexes, and established it as a means of

distinguishing between types of complexes. Cryoscopic and conductimetric experiments have been carried out, but these have much more limited application.

Nomenclature.

The nitrosonium ion is derived from the nitric oxide radical molecule by loss of one electron; by gaining an electron the nitric oxide molecule yields the nitrosyl anion.

Thus:-

$$NO^+ \xrightarrow{+e^-} NO \xrightarrow{+e^-} NO^-$$

nitrosonium ion — nitric oxide — nitrosyl anion

The ionisation potential for the reaction

$$NO \longrightarrow NO^+ + e^-$$

is equal to 9.5 e.v. (Hagstrum & Tate 1941).

This is much lower than the values for nitrogen and oxygen, viz:-

$N_2 \longrightarrow N_2^+ + e^-$ I = 15.5 - 17.2 e.v.

$O_2 \longrightarrow O_2^+ + e^-$ I = 12.2 - 18.2 e.v. depending on the electron state

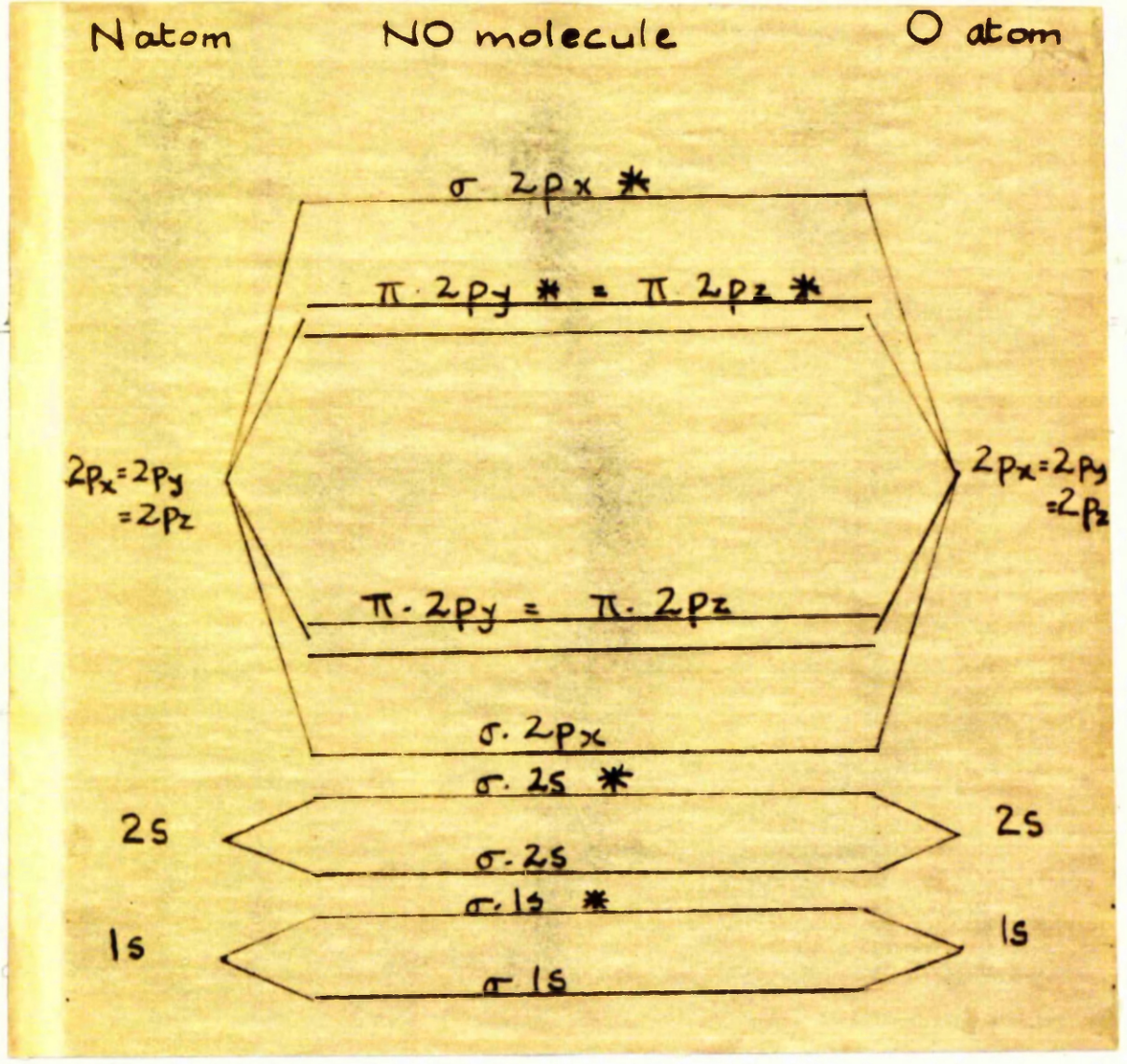
12.2 e.v. (Bartlett 1962)

Hence the nitric oxide molecule loses an electron much more readily than the oxygen or nitrogen molecule. The bond lengths of the species are:-

Nitric oxide	-	1.14 Å
Nitrosonium ion	-	1.06 Å

Pauling's values for the double and triple bond lengths of the N - O bond are 1.18 Å and 1.06 Å respectively, which gives nitric oxide a bond order intermediate between double and triple. Pauling explained this by postulating that the N - O bond in nitric oxide was composed of a double bond plus a three-electron bond. The latter bond would have about half the strength of an electron-pair bond, and would only be energetically feasible when the atoms involved in the bonding are of very similar electronegativities. Loss of an electron from the nitric oxide molecule would convert the 3-electron bond into a normal electron-pair bond, with consequent increase of bond order and shortening of the N - O bond, as observed in the nitrosonium ion. This treatment is fairly satisfactory but a simple molecular orbital approach explains these observations much more elegantly.

Below is given the molecular orbital scheme for the nitric oxide molecule, and its derivation from the nitrogen and oxygen atoms.



The unstarred molecular orbitals are the bonding orbitals, and the starred are the anti-bonding orbitals. The 1s and 2s bonding and anti-bonding orbitals are completely filled and hence these orbitals play no significant part in the N - O bond. The nitrogen and

oxygen atoms contribute 7 electrons, in all, to the molecular orbitals. The bonding sigma 2p orbital can accommodate two, and the degenerate pi-2p(y) and pi-2p(z) can each accommodate two more. Hence one electron must go into the degenerate anti-bonding pi-2p orbitals. The effect of placing electrons in bonding orbitals is to draw the constituent atoms together, while electrons in anti-bonding orbitals force them apart. Hence the presence of one electron in an anti-bonding orbital in conjunction with a triple ($\sigma + 2\pi$) bond will be to increase the bond length somewhat compared to the pure triple bond value. Also, electron loss to yield a cation involves the loss of the anti-bonding electron with consequent shortening of the N - O bond. This is consistent with the data already cited regarding N - O bond lengths in nitric oxide and the nitrosonium ion. Addition of an electron to the nitric oxide molecule to give the nitrosyl anion, NO^-, must involve placement of the extra electron in the anti-bonding pi-2p orbitals; this is evident from consideration of the molecular orbital scheme. This will lengthen the N - O bond still further, and the presence of two electrons in the anti-bonding orbitals will cause considerable bond weakening. This is consistent with the known properties of the nitrosyl anion; compounds in

which this species occurs are much rarer than compounds containing nitrosonium ions.

Being a radical species, the nitric oxide molecule would be expected to dimerise quite readily to give diamagnetic species, that it does not must be largely due to the similar electro-megativities of nitrogen and oxygen, causing the anti-bonding unpaired electron to be well delocalised over the whole molecule. However, in the liquid phase, i.e. between -163°C and -151°C, nitric oxide is known to be very largely dimerised; also the reactions between diethylamine and nitric oxide in ether at-78°C can best be explained by the presence of O = N - N = O dimer molecules. (Drago & Paulik 1960).

The nitrosonium ion is isoelectronic with carbon monoxide and the cyanide anion. The relationship between nitric oxide and carbon monoxide was first noted by Manchot (1910), and extended by the preparation of the 'pseudo-nickel' carbonyls or nitrosyl carbonyls of Hieber and Anderson (1932, 1933), viz:-

$$Fe(NO)_2(CO)_2 \qquad Co(NO)(CO)_3 \qquad Ni(CO)_4$$

In this isoelectronic species, a unit decrease in the atomic number of the metal atom is compensated for by the substitution of a nitric oxide molecule for a carbon

monoxide molecule. The compounds have very similar properties and gradations can be explained by the increased polarity of the nitrosyl (or, strictly speaking, nitrosonium) group.

Although nitric oxide is stable towards dimerisation at ordinary temperatures, it is readily oxidised to give another paramagnetic species, nitrogen dioxide.

$$NO + {}^{1}/_{2}O_2 \longrightarrow NO_2$$

The nitrogen dioxide radical-molecule, is also electronically amphoteric:-

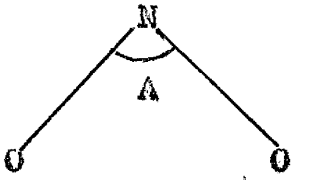
$$NO_2^{+} \xrightarrow{-e^-} NO_2 \xrightarrow{+e^-} NO_2^-$$

nitronium ion — nitrogen dioxide — nitrite anion

$$NO_2 \rightleftharpoons N_2O_4$$

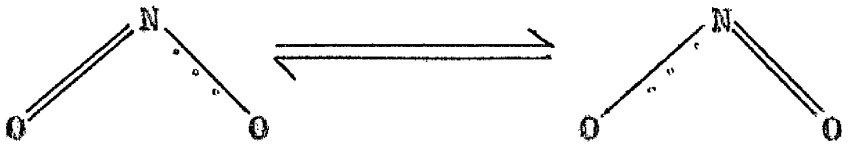
dinitrogen tetroxide

The nitrogen dioxide molecule is bent, viz:-

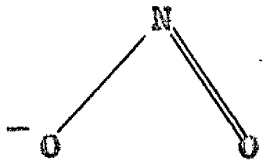


with the bond angle, A, equal to 132 ± 2^{o}, and the N - O bond lengths being both equal to 1.20Å (Claesson et al. 1948); addition of an electron gives the nitrite anion, which is

also bent. In this case the bond angle is between 120° and 130°, and the N - O bond distances are 1.13A (Langseth & Walles, 1934). It is more difficult in this case to construct a molecular orbital energy level scheme similar to the nitric oxide scheme; the simplest representation is the valence bond scheme, involving resonance between the canonical forms:-



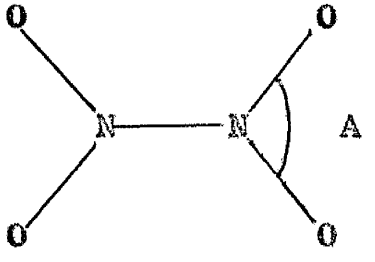
This gives the N - O bond a bond order somewhat less than two, which is in agreement with the measured value of 1.20A cited above. A qualitative molecular orbital picture would place the odd electron in a pi-orbital extending over all three atoms. In a molecular orbital treatment of this molecule the unpaired electron is placed in a slightly anti-bonding orbital (Green & Linnett 1961). The short bond lengths in the nitrite anion suggests some degree of triple bonding between nitrogen and oxygen and this is difficult to explain in terms of canonical forms such as:-



which would give rise to a much greater N - O bond length. The nitrite anion is much more stable and much better characterised than its analogue in the nitric oxide system, the nitrosyl anion.

Loss of an electron from the nitrogen dioxide molecule gives the linear intronium cation NO_2^+, isoelectronic with carbon dioxide. The bond length N - O, is 1.18Å (Eriks 1950), identical to the calculated value for an N - O double bond, so that this is consistent with the formulation:-

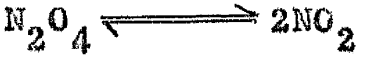
Nitrogen dioxide readily dimerises at ordinary temperatures to dinitrogen tetroxide, N_2O_4, and the extent of dimerisation increases with decreasing temperature. In the solid state the structure is:-



A = 126°
N - N = 1.64Å
N - O = 1.17Å

(Broadley et al. 1949)

and the liquid can be considered as an equilibrium:-



This will be largely due to the absence of the unpaired electron in the latter case. Since both nitric oxide and nitrogen dioxide are radical molecules there should be a stabilisation in the latter case, due to the greater possible delocalisation of the odd electron. With removal of the unpaired electron this is no longer the case.

Both the nitrosonium and nitronium ions are very susceptible to hydrolysis

$$NO^+ + H_2O \rightleftharpoons H^+ + HNO_2 \rightleftharpoons 2H^+ + NO_2^-$$

$$NO_2^+ + H_2O \rightleftharpoons H^+ + HNO_3 \rightleftharpoons 2H^+ + NO_3^-$$

and Millen (1950b) has shown that the nitronium ion is much less stable to hydrolysis than the nitrosonium ion; the latter is virtually unaffected by concentrations of water which will completely hydrolyse the former. As the above equilibria imply, nitrosonium and nitronium ions are formed in systems of high acidity containing respectively nitrite or nitrate ion.

Systems containing nitrosonium ions, under high pressures of nitric oxide give species with one-electron bonds (Seel et al. 1953; Seel & Sauer 1957).

$$NO^+ + NO \rightleftharpoons N_2O_2^+$$

This cation dissociates readily in the absence of nitric oxide but is stable for appreciable lengths of time at normal temperatures and pressures in solutions of high viscosity. It exists in two isomeric forms, corresponding to different electronic states, one form being blue, the other red. It is probable that this cation is responsible for the blue colour of the 'chamber crystals' of the lead chamber process.

An analogous cation, $N_2O_3^+$, formed by the equilibrium

$$NO^+ + NO_2 \rightleftharpoons N_2O_3^+$$

seems probable (Goulden & Miller 1950). The cation $N_2O_3^+$ has two possible canonical forms:-

$$\overset{+}{NO} \cdot NO_2 \quad (1) \qquad \text{and} \qquad NO \cdot \overset{+}{NO_2} \quad (11)$$

and Goulden & Millen cite Raman spectroscopic evidence for the predominance of species (1)

The nitrosonium ion also appears to solvate in nitrosyl chloride solution (Burg & MacKenzie 1952) and in acetonitrile solution (Fraser & Dasent 1960) but the species formed probably involve normal electron-pair bonds.

The types of compound involving nitrosonium ions or the nitrosyl group have been reviewed by Addison & Lewis (Quart. Revs. 1955); the main types are

1. Nitrosonium Salts $NO^+ \ X^-$

   These contain the free nitrosonium ion; examples are $NO^+ \ BF_4^-$, $NO^+ \ ClO_4^-$.

2. Compounds in which the NO^+ group is bonded to a metal atom $M \leftarrow \overset{+}{N}O$

In this case the nitric oxide molecule formally donates one electron to the metal and then forms a metal - nitrosyl bond; almost invariably bonding to the metal occurs via the nitrogen atom but some instances have been reported in which bonding to the metal is postulated to occur via the oxygen (Yamada et el 1960); also, the compound $(C_3H_7) - Zn - O - N\begin{matrix} C_3H_7 \\ NO \end{matrix}$ has been postulated to form via a $\begin{matrix} C_3H_7 \\ C_3H_7 \end{matrix}\!\!>\!Zn - O = N$ intermediate (Abraham et al 1962). An example of this type of compound is cobalt nitrosyl tricarbonyl, which was mentioned previously in connection with the 'pseudo' nickel' carbonyls. In this type of compound two types of electron interchange are believed to occur between the nitrosonium ion and the metal atom:-

1. Sigma-donation from the nitrosonium ion to the metal. This will have the effect of placing an excessive negative charge on the metal atom which could be relieved by

11) 'Back-donation' from the metal d-orbitals to the vacant anti-bonding pi-orbitals of the nitrosonium ion, which are of a suitable size and symmetry to participate in this form of bonding.

This multiple bonding is believed to contribute largely to the facility with which nitric oxide behaves as a ligand.

3. Compounds in which the nitrosyl anion bonds to a metal atom.

These are much less common than those of groups 1. and 2; the lower stability of the nitrosyl anion is responsible for this. The unstable iron nitrosyl $Fe(NO)_4$ is believed to have the structure:-

$$(\overset{+}{NO})_3 \longrightarrow Fe \longleftarrow \overset{-}{NO} \quad \text{(Griffith et al. 1958b)}$$

The co-ordinated nitrosyl anion is also believed to occur in the nitrosopentamonine cobalt salts $[Co(NH_3)_5(NO)]\ X_2$, which can occur in two forms, viz, a black form originally believed to contain dimeric cationic species and co-ordinated nitrosyl anions and nitrosonium ions, and a red series containing the monomeric cation

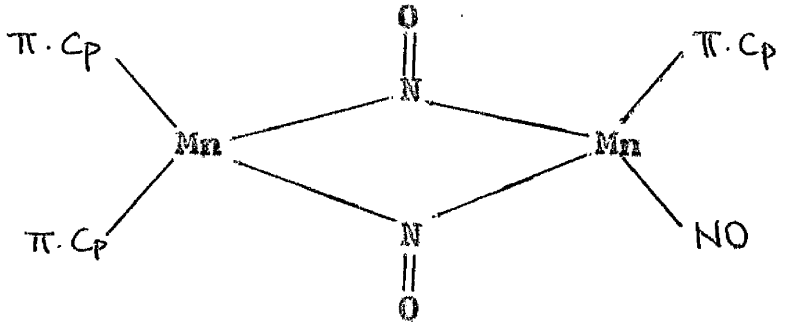
with all the NO grouping present as the nitrosyl anion (Griffith et al. 1958a). However, a recent examination of the conductivity of solutions of the red isomer has shown that it is dimeric; the black isomer was too unstable to examine by these means (Feltham 1964).

As will be explained later in this chapter, infrared spectroscopy can distinguish between these three possibilities, usually without any ambiguity.

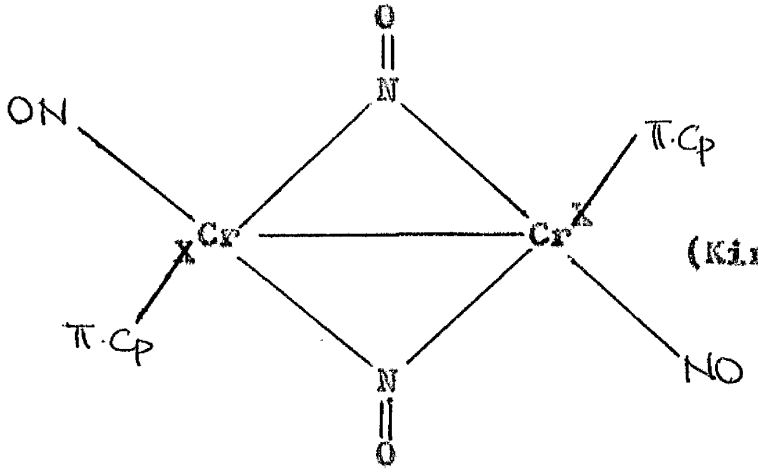
Other significant types of compound containing the nitrosyl grouping are

4. Compounds containing a bridging nitrosyl group.

Besides behaving as a cationic or anionic donor ligand, nitric oxide can also behave as a bridge in binuclear complexes. Again the nitric oxide molecule can be considered as losing an electron to the metal atom centres, and the effective donor group is the nitrosonium ion. Few compounds of this structure are known, the first to be prepared being $(C_5H_5)_3\ Mn_2\ (NO)_3$. (Piper and Wilkinson 1956)



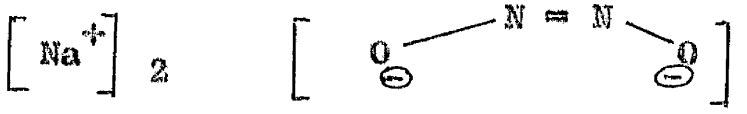
Again, as in the majority of nitrosyl metal complexes, bonding from the nitrosyl group occurs via the nitrogen atom. Recently, a cyclopentadienyl nitrosyl complex of chromium has been prepared, believed to contain bridging nitrosyl groups; also, in this case the chromium - chromium bond is believed to be short enough for metal-metal bonding to occur:-



Structures involving bridging nitrosyl groups have been assigned in the above cases on the basis of infrared evidence.

5. The free nitrosyl anion has been postulated to occur in 'sodium nitrosyl', a compound first prepared by Zintl & Harder (1933) and postulated as being $Na^+ NO^-$ on the basis of its diamagnetism (Frazer & Long 1938). The method of preparation involved treatment of a sodium/ ammonia solution with dry nitric oxide, a white solid

separating out; when Goubeau & Laitenberger (1963) repeated this they found that this compound was identical with sodium hyponitrite $Na_2N_2O_2$, which they depicted as:-



This compound would be expected to be diamagnetic; by examination of the molecular orbital scheme for nitric oxide, it can be seen that the NO^- anion would be expected to be paramagnetic, like the oxygen molecule with which it is isoelectronic. The two unpaired electrons in both the nitrosyl anion and the oxygen molecule are in the two degenerate pi-antibonding orbitals; unless the energy of electron pairing is abnormally low, Hund's Rule will operate and the electrons will occupy different orbitals and thus possess parallel spins.

Hence, the existence of the free nitrosyl anion is still in question.

6. It is possible that some compounds exist in which the nitric oxide molecule donates two electrons to a metal atom or ion and retains an unpaired electron. Such a structure would be:-

if the metal centre was paramagnetic, there would be two paramagnetic centres in the molecule, but no compounds

have been prepared which could be assigned such a structure.

As emphasised before, in practically all cases where metal - nitrosyl bonding occurs, the linkage occurs via the nitrogen atom; also the systems

M - N = O

are always linear.

Nitrogen dioxide is a much less versatile group than nitric oxide, and the compounds of main interest in this work are those containing the free nitronium ion, NO_2^+: This has been well characterised by Ingold and his school in a series of papers in 1950.

Nitrogen dioxide will behave as a ligand, bonding, like the nitric oxide molecule, via the nitrogen atom. The co-ordinated nitrogen dioxide molecule is bent, and has the same symmetry properties as the nitrite ion, NO_2^-, (Gatehouse 1958). No instances are known in which the nitronium ion behaves as a ligand.

Formation of nitrosonium ions and nitronium ions.

Systems in which the nitrosonium or nitronium ion occurs, or can be produced, are as follows:-

1. Electric Discharge.

Passage of an electric discharge through nitric oxide at low pressure causes ionisation; the ionisation potential for this reaction is 9.5 e.v. The method is of

no importance in the synthesis of nitrosonium salts or nitrosyl complexes.

2. Self ionisation of nitrosylating solvents

Nitrosyl chloride is believed to ionise in the liquid phase, viz

$$NOCl \rightleftharpoons NO^{+} + Cl^{-}$$

By following the rate of chlorine exchange in the systems nitrosyl chloride/tetra-ethyl or methyl ammonium chloride, using radioactive chlorine, Lewis and Wilkins (1955) concluded that the data could best be explained by transfer via chloride ions and postulated the equilibrium $NOCl \rightleftharpoons NO^{+} + Cl^{-}$. Nitrosonium ions probably exist to some extent in solid nitrosyl chloride, the extent of ionisation being inversely proportional to temperature. Liquid nitrosyl chloride is deep red, as is solid nitrosyl chloride at -78°C, but the colour lightens gradually until at -196°C it is pale yellow. The nitrosonium ion, itself, is colourless, and any colour in simple nitrosonium systems can be explained by charge transfer reactions of the type:-

$$\dot{N}\,O^{+} \quad X^{-} \longleftrightarrow \dot{N}O \quad \dot{X}$$

and it is this mechanism which causes the deep colours of the nitrosyl halides. Hence although nitrosyl chloride

is primarily covalent, some self ionisation may occur. The same applies to nitrosyl bromide, NOBr.

Further evidence that self ionisation may occur comes from the structures of nitrosyl chloride and bromide; these both have the structure:-

Nitrosyl chloride	Nitrosyl bromide	
1.14A	1.15A	Band Length N - O
1.95A	2.14A	" " N - X
116°	117°	Bond angle X - N - O

For nitrogen-halogen single bonds, the radius sum values are 1.73A (N - Cl) and 1.88 (N - Br); thus in the nitrosyl halides the nitrogen - halogen bonds are weaker than single bonds, and it is quite possible that self ionisation will occur. (Ketelaar & Palmer 1937).

As previously stated, dinitrogen tetroxide dissociates in the liquid state

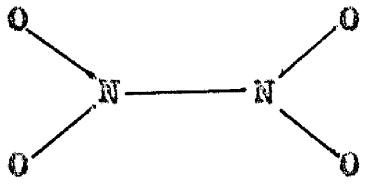
$$N_2O_4 \rightleftharpoons 2NO_2$$

Besides this, there are two self-ionisations theoretically possible also:-

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^-.$$

though the latter one does not appear to occur, in practice. This is unusual, since the structure of the dinitrogen tetroxide molecule is:-



(Broadley & Robertson 1949) - solid state.

(Smith & Hedberg 1956) - gas phase.

The specific conuctance has been determined, and is very small; $K = 1.3 \times 10^{-12}$ ohm^{-1} cm^{-1} compared to water 4×10^{-8} ohm^{-1} cm^{-1} at the same temperature (18°C). (Addison et al 1951a).

In anhydrous nitric acid, dinitrogen tetroxide dissociates almost completely into nitrosonium and nitrate ions; no evidence was found for the ionisation

$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^-$$

and the dissociation into nitrogen dioxide species was extremely small (Millen & Watson 1957).

The equilibria

$$NO^+ + OH^- \rightleftharpoons HNO_2 \rightleftharpoons H^+ + NO_2^-$$

have been mentioned.

Since dinitrogen trioxide, N_2O_3, is formally the anhydride of nitrous acid, it would be expected that in strongly acid solutions, it would give nitrosonium ions. This is the case. The following ionisation has been established:-

$$N_2O_3 + 3H_2SO_4 \longrightarrow 2NO^+ + H_3O^+ + 3HSO_4^-$$

by cryoscopic measurements (Gillespie et al 1950a) and confirmed by Raman observations (Millen 1950b).

By analogy with the above, dinitrogen tetroxide would be expected under similar conditions, to give a mixture of nitrosonium and nitronium ions, since it is the mixed anhydride of nitrous and nitric acids. Also dinitrogen pentoxide, N_2O_5, should yield nitronium ions only. The same workers found this to be the case and the following ionisations were verified:-

$$N_2O_4 + 3H_2SO_4 \longrightarrow NO^+ + NO_2^+ + H_3O^+ + 3HSO_4^-$$

$$N_2O_5 + 3H_2SO_4 \longrightarrow 2NO_2^+ + H_3O^+ + 3HSO_4^- \quad : \text{(Gillespie et al 1950b)}$$

In addition to this, dinitrogen pentoxide behaves as a binary electrolyte in absolute nitric acid, ionising thus:-

$$N_2O_5 \rightleftharpoons NO_2^+ + NO_3^- \qquad \text{(Gillespie et al 1950b).}$$

This was an extension of earlier work on the nitric acid/sulphuric acid system which established the ionisation

$$HNO_3 + 2H_2SO_4 \longrightarrow H_3O^+ + NO_2^+ + 2HSO_4^-$$

(Gillespie et al 1946),

and also from pioneer work by Hantzsch (1925) and Hantzsch & Berger (1928). These latter workers studied the nitric acid/sulphuric acid and nitric acid perchloric acid systems and obtained compounds which they formulated as

$$[H_2NO_3^+][ClO_4^-] \quad \text{and} \quad [H_2NO_3^+][HSO_4^-]$$

Goddard et al (1950) repeated this work with perchloric acid and found that the compound $H_2NO_3^+ \cdot ClO_4^-$ could be separated into nitronium perchlorate $NO_2^+ \cdot ClO_4^-$ and hydroxonium perchlorate $H_3O^+ \cdot ClO_4^-$, and no evidence existed for the presence of $H_2NO_3^+$ species, either from cryoscopic or Raman spectroscopic data. This was confirmed for the system $HNO_3/H_2S_2O_7$ by Millen (1950a) who observed the Raman spectra of such solutions at varying concentrations.

The production of nitronium ions in strong acid systems in the manner described above has been utilised by Kuhn (1962) to prepare nitronium salts of the fluoborate, fluophosphate and fluoarsenate anions, viz:-

$$2HF + HNO_3 \rightleftharpoons NO_2^+ + H_3O^+ + 2F^-$$ (Gillespie & Millen 1947).

This equilibrium is exactly analogous to the ionisation of nitric acid in sulphuric acid. By addition of boron trifluoride, the reaction

$$BF_3 + F^- \longrightarrow BF_4^-$$

occurs and nitronium fluoborate is obtained. In practice the reaction is carried out in nitromethane solution and the reaction is

$$HF + 2BF_3 + HNO_3 \longrightarrow NO_2BF_4 + H_2O.BF_3$$

Similarly sodium nitrite has been employed as a source of nitrosonium ions in the formation of certain metal nitrosyl complexes, viz:-

A stoicheimetric excess of sodium nitrite will react with bis (triphenylphosphine) nickeldibromide to give bis (triphenylphosphine) nickelnitrosylbromide, $[(C_6H_5)_3P]_2NiNOBr$, among other products. (Feltham 1960); infrared evidence assigns an Ni ◁—NO^+ linkage to this compound. Although the reaction was not carried out in strongly acid solution, the prescribed conditions for obtaining nitrosonium ion from nitrite ion, the sodium nitrite must have been the source of nitrosonium ion.

Diagnostic Methods for nitrosonium ions.

1. Cryoscopy.

Besides the applications referred to above in the elucidation of the species present in nitric acid/strong acid systems, this method is historically interesting in that Hantzsch, on the basis of cryoscopic studies on nitrosyl hydrogen sulphate solutions in sulphuric acid, first postulated the existence of the nitrosonium ion species. He postulated the ionisation:-

$$NOHSO_4 \longrightarrow NO^+ + HSO_4^- \qquad \text{(Hantzsch 1909)}$$

In cases such as

$$N_2O_3 + 3H_2SO_4 \longrightarrow 2NO^+ + 3HSO_4^- + H_3O^+$$

the value of the van't Hoff factor i enables the number of ionic species produced per molecule of dinitrogen trioxide to be obtained, and cryoscopy can distinguish between possible reaction paths which yield differing numbers of ionic species. The most notable case of this occurs in the nitric acid/perchloric acid system, in which Hantzsch postulated the ionisation

$$HClO_4 + HNO_3 \longrightarrow H_2NO_3^+ + ClO_4^-$$

giving two ions per nitric acid molecule.
Goddard et al. (1950) showed that the following ionisation occurred:-

$$2HClO_4 + HNO_3 \longrightarrow H_3O^+ + NO_2^+ + 2\,ClO_4^-$$

giving four ions per nitric acid molecule.

2. Conductivity and electrolytic data.

The compounds $NO.AlCl_4$, $NO.FeCl_4$ and $NO.SbCl_6$ dissolve readily in nitrosyl chloride solution to give strongly conducting solutions (Burg & Campbell 1948); this indicates that ionisation occurs in solution though it does not necessarily infer that the solids are ionic.

Equilibrium studies provided evidence for the existence of $NOAlCl_4$. NOCl and NOFeCl4.NOCl species, and these were interpreted as compounds in which the nitrosonium ion is solvated by nitrosyl chloride (Burg & MacKenzie 1952). The extremely high transport number calculated for the nitrosonium ion in nitrosyl chloride solution implies the existence of a chain transfer mechanism analogous to that occurring in the electrolysis of water.

Dinitrogen tetroxide yields nitrosonium nitrate-complexes, viz:-

$Zn(NO_3)_2 + 2N_2O_4 \longrightarrow (NO^+)_2\ (Zn(NO_3)_4^{2-})$ (Addison et al 1951b). When a solution of nitrosonium tetranitratozincate is dissolved in nitromethane, electrolysis liberates nitric oxide at the cathode. The same salt will undergo acid-base reactions with anhydrous nitrates and these can be followed conductimetrically:-

$$(NO^+)_2\ (Zn(NO_3)_4^{2-}) + 2(C_2H_5NH_3^+\ NO_3^-) \longrightarrow$$

$$(C_2H_5 \cdot NH_3^+)_2 \cdot (Zn(NO_3)_4^{2-}) + 2N_2O_4$$ (Addison & Hodge 1954a)

A reaction such as this also characterises the anion of the nitrosonium salt.

3. Magnetic susceptibilities

Asmussen (1939) assembled magnetic data on several metal chloride-nitrosyl chloride adducts and classified them according to their molar susceptibilities and the apparent or 'induced' molar susceptibility of the attached nitrosyl chloride. In no instances were definite structure assignments possible. The compounds giving low 'induced' molar susceptibilities for nitrosyl chloride were the adducts $ZnCl_2$.NOCl, $HgCl_2$.NOCl and $MnCl_2$.NOCl. All these are thermally unstable with respect to dissociation and Asmussen formulated them as molecular addition compounds. The adducts $SnCl_4$.2NOCl and $PtCl_4$ 2NOCl were found to give much higher induced molar susceptibilities for the attached nitrosyl chloride and were formulated as ionic nitrosonium salts; these were also more stable thermally.

4. Chloride Exchange.

Zinc, cadmium and mercuric chlorides react with liquid nitrosyl chloride to give insoluble adducts. The rate of chloride exchange between nitrosyl chloride and the adduct has been followed (Lewis & Sowerby 1956), and they found that rapid exchange occurred between absorbed nitrosyl chloride and the metal chloride, while slow heterogeneous exchange occurred between absorbed and liquid nitrosyl chloride. To account for this, the formation of MCl_3^- species (M = Zn, Cd, Mg) was postulated and hence NO^+ MCl_3^- were considered to be produced. The anions of the type MCl_3^- were postulated to be polymeric species; this will be considered later.

The systems $AsCl_3$/NOCl and $POCl_3$/NOCl were studied; a slow exchange in the latter case indicated lack of compound formation, while a rapid rate in the $AsCl_3$/NOCl case, together with equilibrium studies, suggested an adduct $AsCl_3 . 2NOCl$ which was postulated as being $(NO^+)_2 (AsCl_5)^{2-}$ or $NO.NOCl^+ AsCl_4^-$ (Lewis & Sowerby 1957). This will be dealt with further, in a later section.

5. Infrared and Raman Spectroscopy.

By studying the Raman spectra of nitrosyl hydrogen sulphate in sulphuric acid/water solutions, Angus & Leckie (1935) assigned a displacement of 2340 cm^{-1} to the nitrosonium ion. The intensity of the band was highly dependent of the concentration of sulphuric acid and became very strong above a sulphuric acid concentration of over 70%; the position of the band also depended slightly on the sulphuric acid concentration, occurring at a higher frequency as the concentration increased. The observed displacement was found to be similar to that recorded for the isoelectronic nitrogen molecule, and solid nitrosyl hydrogen sulphate was found to give a Raman displacement of 2311 cm^{-1}.

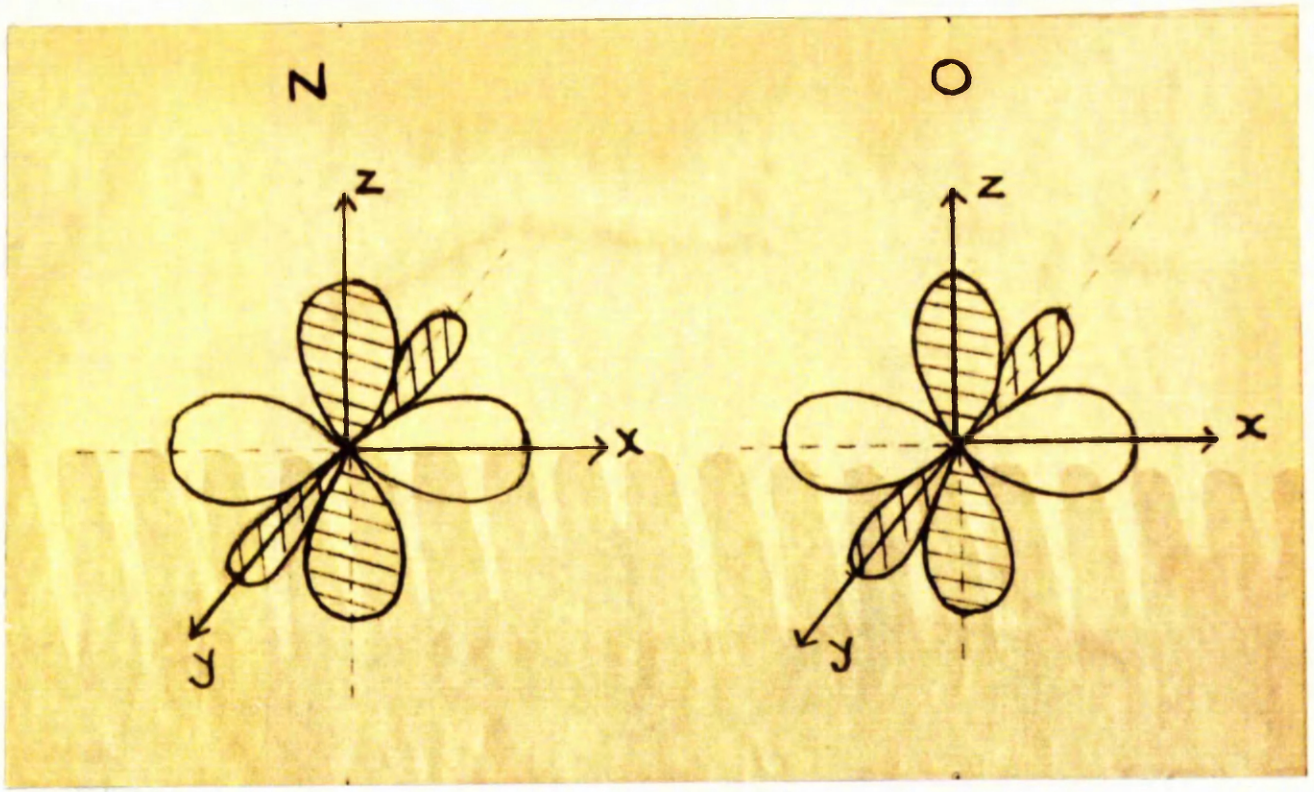
Nitric oxide itself absorbs at 1877 cm^{-1} (Addison & Lewis 1955) and nitrosyl chloride gives a band due to the -N=O bond at 1799 cm^{-1} (Burns & Bernstein 1950); these are both infrared bands.

Gerding & Houtgraaf (1953) have shown that the adduct $AlCl_3$.NOCl gives a Raman displacement of 2236 cm^{-1}, which is of the same order as Angus & Leckie's value for nitrosyl hydrogen sulphate; in addition, the same compound gives a low frequency Raman band identical to that in $AlCl_3$. NaCl . This presumably indicates the presence of the $AlC4^-$ ion in both cases.

Lewis, Irving & Wilkinson (1958) describe a series of complexes which are regarded as involving nitrosonium ion - metal co-ordination and these all give prominent infrared absorptions in the 1580 - 1930 cm^{-1} region. Complexes of the type in which the nitrosyl anion is the ligand absorb at a much lower frequency, in the region of 1100 cm^{-1} (Griffith et al 1958, a, b). The compound $(C_5H_5)_3 Mn_2 (NO)_3$, mentioned before as possibly containing bridging nitrosyl groups gives an infrared absorption at 1510 cm^{-1} (Piper & Wilkinson 1956).

From the molecular orbital scheme constructed for the nitric oxide molecule, it is evident that the N - O bond in the nitrosonium ion, consisting of a sigma and two pi-bonds, is stronger than the N - O bond in nitric oxide which is weakened by the odd electron having to go into the pi-antibonding orbital. Hence the former is shorter and would be expected to give a higher vibrational frequency.

The nitrosonium ion is isoelectronic with the nitrogen molecule, and the total number of 2s and 2p electrons in both cases is ten. They can both be considered to be built up as follows, on the basis of both atoms being in an sp hybridized state.



The orbitals shaded are those participating in pi-bonding (the $2p_y$ and $2p_z$ orbitals). One of the sp hybrid orbitals on each atom overlaps to give what is equivalent to the sigma-bonding orbital. Two electrons are involved in this. The py and pz orbitals on each atom overlap to give the pi-bonding molecular orbitals. Thus six electrons have been used in the N - O bond and the other four available electrons go into the two vacant sp orbitals, one on each atom. It is this orbital on the nitrogen atom which is responsible for the nitrosonium ions donor properties. These sp orbitals not involved in bonding between the atoms could be equivalent to the antibonding s orbitals of the molecular orbital energy level scheme.

When the nitrosonium ion donates these two electrons to a metal ion, the latter is believed to get rid of some of the excess negative charge thus acquired via back-donation from the metal d - orbitals to the vacant pi - antibonding orbitals which are of suitable shape and symmetry for this. The presence of electrons in the antibonding orbitals will lengthen the N - O bond and lower the vibrational frequency. The further lowering of the vibrational frequency in complexes involving nitrosyl anions is just an extension of this. In this case, little or no metal ——→ligand back-bonding can be expected to occur since the acceptor orbitals on the nitrosyl anions are already occupied; and this will lengthen the N - O bond and lower the vibrational frequency of the mode.

The cases of nitrosyl chloride and complexes involving bridging nitrosyl groups are slightly different; whereas the metal - N = O bonding system in the above cases are linear, these other cases involve bent X - N = O systems. On a valence band treatment this requires the nitrogen atom to have considerable sp^2 character. This will lessen the pi-bonding character between nitrogen and oxygen, lengthening the bond, and lowering the frequency.

The nitric oxide molecule and its derivatives have only one vibrational frequency, that corresponding to bond stretching and it is both Raman and infrared active.

The data can be summarised:-

Type of compound	Vibrational frequency region
Nitrosonium salt ($NO^+ X^-$)	2200 - 2400 cm^{-1}
Nitrosonium donor complex ($M \leftarrow NO^+$)	1580 - 1930 cm^{-1}
Bridging nitrosyl complex	c. 1500 cm^{-1}
Nitrosyl donor complex	1050 - 1200 cm^{-1}

Infrared data can usually be used to assign structures to nitric oxide compounds, with little ambiguity. Difficulty may arise when systems containing nitronium ions are examined.

As mentioned before, the nitronium ion is linear:-

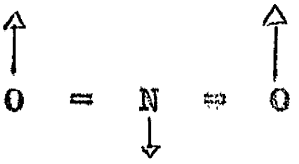
$$\left[O = N = O\right]^+$$

It has three vibrational modes:-

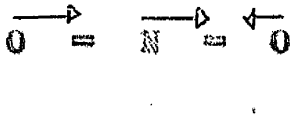
$O \overset{\leftarrow}{=} N \overset{\rightarrow}{=} O$ $\quad \nu_1$ Symmetrical stretch

Raman active

infrared inactive.



V_2 - deformation — Raman active, infrared active



V_3 - asymmetric stretch — Raman inactive, infrared active

These modes occur at the following frequencies:-

$V_1 V_1$ - 1400 cm^{-1} (Ingold, Millen & Poole 1950)

V_3 - 2350-2400 cm^{-1}

V_2 - 538 cm^{-1} Teranishi & Decius 1954

The infrared spectrum of the nitronium ion usually consists of bands in the following regions, with the assignments given.

c.540 cm^{-1}	weak - medium	(V_2)
2350 - 2400	strong	(V_3)
3750 - 3800	weak	(V_1 & V_3)

Thus, in the presence of bands which could overlap the V_2 and (V_1 + V_3) modes the only prominent band is the V_3 fundamental, lying in the same region as that for the free nitrosonium ion; hence ambiguity is possible.

Obviously if Raman spectra are available the presence of the 1400 cm^{-1} band would definitely confirm the presence of nitrosonium ion.

6. X-ray Crystallography.

Several compounds are known which from their stoicheiometry would be expected to contain the nitrosonium ion. Klinkenberg (1937, 1938) studied the X-ray powder photographs of the compounds $NO.BF_4$, $NO.ClO_4$, $SnCl_4.2NOCl$ and $PtCl_4.2NOCl$, and compared them with the potassium analogues. In all cases the complexes were isomorphous with the potassium analogues. Since the potassium salts all contain the potassium ion, it must be assumed that the complexes contain the nitrosonium ion. This ion is formally cylindrical but by rotation in the lattice spherical symmetry can be obtained. By comparison of nitrosonium fluoborate and perchlorate with the isomorphous hydronium and ammonium compounds, Klinkenberg also calculated the effective radius of the nitrosonium ion in free rotation to be 1.40 Å ; this makes it larger than the ammonium ion and very similar to the hydronium ion.

Obviously this method only verifies the existence of nitrosonium ions in compounds which have known ionic analogues, and is thus limited in application.

CHAPTER I

STUDIES ON PREVIOUSLY REPORTED NITROSONIUM FLUORO AND CHLORO-ADDUCTS

As mentioned in the introduction, several metal and non-metal chlorides will react with nitrosyl chloride to form adducts. (Gall & Mengdehl 1927; Rheinboldt & Wasserfuhr 1927; Klinkenberg 1938; Partington & Whynnes 1948, 1949). In addition, nitrogen oxides are known to react with sulphur dioxide or sulphur trioxide to yield products. (Hart-Jones 1929; Goddard et al 1950; Lehmann & Klüge 1951; Gerding & Eriks 1952). In addition, several nitrosonium and nitronium fluoro-metal or non-metal compounds have been formed. (Woolf & Emeleus 1950; Woolf 1950; Robinson & Westland 1956; Clark & Emeleus 1958; Geichmann et al 1962, 1963). All of these compounds can be formulated as containing nitrosonium or nitronium ions and some have been shown to do so, by the methods of x-ray crystallography (Klinkenberg 1937, 1938), Raman spectroscopy (Gerding & Eriks 1952, Gerding & Eriks 1953) and infra-red spectroscopy (Geichmann et al 1962, 1963). It is possible to examine all the adducts by infra-red

spectroscopy, and in the present work, this was used as a means of determining the bonding state of the nitrosyl group in the compound. As stated in the introduction, compounds containing the free nitrosonium ion should absorb in the infra-red region at about 2200-2400 cm^{-1}, those containing this cation bonded to a metal atom at 1580-1930 cm^{-1} and those containing a metal-nitrosyl anion bond at 1050-1200 cm^{-1}. These ranges of frequency are sufficiently separate to enable the bonding state to be determined unambiguously.

The compounds studied, with their nitrosonium ion stretching frequencies are tabulated on the following page, together with data obtained by other workers. In addition, x-ray data were obtained for the majority of the compounds and compared with x-ray data for the potassium analogues, where possible, to establish whether or not isomorphism occurred.

The infra-red Raman data shows that all the compounds listed can be classified as nitrosonium salts, though the absorption range of the free nitrosonium ion is very large, being nearly 250 cm^{-1}.

X-ray data on the nitrosonium and potassium salts which are isomorphous are tabulated elsewhere in this chapter (table 2); and spectroscopic data on the anions studied are tabulated in tables 3 ⟶ 5 .

The compounds tabulated in table 1 will be discussed separately (regarding their structure, etc.) starting with those giving high frequency absorptions. General statements and conclusions will be made at the end of the chapter.

$(NO)_2GeF_6$

This is not isomorphous with the potassium analogue K_2GeF_6; the infra-red spectrum shows two bands in the free nitrosonium ion region, the main band at 2391 cm^{-1} with a shoulder at 2336 cm^{-1}. Gerding & Eriks (1952) have shown that the compound (NO) (NO_2) (S_3O_{10}) gives two Raman peaks at 2277 cm^{-1} and 2308 cm^{-1} and assigned the former peak to the antisymmetrical (V_3) mode of the nitronium ion, rendered Raman active by the ion-site symmetry in the crystal lattice. In view of the analytical data for $(NO)_2GeF_6$ it is most unlikely that the same explanation holds; also, since the reaction system was nitrosyl chloride/germanium dioxide/ bromine trifluoride, and the nitrosyl chloride was spectroscopically free from dinitrogen tetroxide, it is improbable that any mechanism for the formation of nitronium ions existed. It was not possible to check the absence of nitronium ion by observing the infra-red regions where the ($V_1 + V_3$)

and V_2 vibrational modes were expected, due to the rapidity with which $(NO)_2GeF_6$ attacked nujol. The (V_1+V_3) region was examined in florube, and no evidence was found for nitronium ion. Hence the most probable explanation is that the nitrosonium ion in $(NO)_2GeF_6$ occupies two different types of lattice site, so that it is in two positions of different local symmetry.

$(NO)_2GeF_6$ is extremely hygroscopic, decomposing rapidly even in the 'dry-box' with copious nitrogen dioxide evolution leaving a germanium dioxide residue. In vacuo, and in the complete absence of moisture it is quite stable, and is thermally stable.

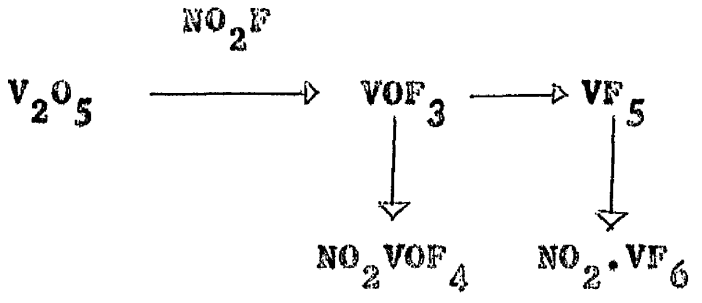
$(NO)\ VF_6$

This compound, like $(NO)_2GeF_6$, is not isomorphous with its potassium analogue $K.VF_6$, and also gives two infra-red bands; one at 2391 cm^{-1}, with a shoulder at 2328 cm^{-1}. The explanation is likely to be similar to that in the instance of $(NO)_2GeF_6$, the nitrosonium ion being present in two different types of lattice position.

Like $(NO)_2GeF_6$ it is extremely hygroscopic and rapidly hydrolyses in air to leave a vanadium pentoxide residue; it is quite stable in vacuo.

The reaction nitrosyl chloride/vanadium pentoxide/bromine trifluoride gives $NO.VF_6$ without any contamination by $NO.VOF_4$; if a metal cation, such as sodium, is substituted for the nitrosonium cation, the main product is $Na.VOF_4$, and even prolonged refluxing in bromine trifluoride will not give pure $Na.VF_6$. (Sharpe & Woolf 1951). The preparation of the sodium salt of the hexafluorovanadate ion requires that vanadium chloride be used instead of vanadium pentoxide in the preparation; under these conditions pure $Na.VF_6$ results.

Aynsley et al (1954) reported the following reaction scheme for the vanadium pentoxide/nitryl fluoride systems:-



This demonstrates that the nitronium ion system can give both the fluovanadate and the oxyfluovanadate. This type of reaction has not been repeated using nitrosyl fluoride, due to the difficulty of handling this reagent, so that the compound $NO.VOF_4$ is as yet unknown.

Recently, reaction of nitric oxide or nitrogen dioxide with vanadium pentafluoride suggests that $NO^+ VF_5^-$ and $NO_2^+ VF_5^-$ species may be formed, though the reactions

$$NO_x + VF_5 \longrightarrow NOVF_6 + VF_4 \qquad (x = 1 \text{ or } 2)$$

occur more readily than

$$NO_x + VF_5 \longrightarrow NO_x \cdot VF_5$$

(Ogle et al 1964).

$\underline{NO.BF_4}$

This compound was shown to be isomorphous with potassium fluoborate by Klinkenberg (1937), and this was confirmed in the present work. The x-ray data reported latterly (Sharp & Thorley 1963) were incorrect and the corrected data are given in table 2; the values show a reasonable agreement with those of Klinkenberg.

The stretching frequency for the nitrosonium ion is considerably at variance with that given by Sprague et al (1960) and Evans (1963). Evans reports that the nitronium ion V_3 frequency in $NO_2.BF_4$ is 2387 cm^{-1}, and suggested that the value obtained in the present work was due to this same mode, the nitronium ion being present as an impurity. However, x-ray data submitted by the same worker for the nitrosonium salt, were identical with

data obtained in the present work. It is most unlikely that nitrosonium and nitronium fluoborates have the same unit cell sizes; thus the compounds in both cases must have been pure nitrosonium fluoborate and the explanation must lie elsewhere.

Incidentally, the nitronium ion V_3 frequency reported by Evans does disagree somewhat with the value of 2358 cm^{-1} obtained by Cook (1960).

The x-ray data show that substitution of nitrosonium ion for potassium ion in a fluoborate lattice increases the unit cell dimensions slightly. The volume of the unit cell increases, due to the accommodation of the larger nitrosonium ion. The nitrosonium ion is cylindrical, but it can obtain spherical symmetry when it is allowed to rotate freely in a lattice, and under these conditions, the effective radius is 1.40Å (Klinkenberg 1937), which is larger than the value r = 1.33Å, for the potassium ion. Hence an increase in unit cell size would be expected.

$NO.SbF_6$

This compound is not isomorphous with its potassium analogue; unlike the vanadate and germanates it gives quite a broad absorption in the

nitrosonium ion region. Again, the existence of a prominent shoulder indicates that two types of nitrosonium lattice site are present in the unit cell.

This reacted much less rapidly with nujol than did $(NO)_2GeF_6$ and $NO.VF_6$, and it was possible to obtain data on the SbF_6^- anion; this was found to absorb at 660 cm^{-1}, in good agreement with a value of 660 cm^{-1} for the potassium salt (Peacock & Sharp 1959). (See table 5).

$NO.PF_6$

This compound gave a single sharp absorption at 2379 cm^{-1} in the infra-red region; it was not isomorphous with potassium fluophosphate.

Table 5 tabulates data obtained in the present work on the PF_6^- anion in the nitrosonium salt, and by other workers, with other cations. In all cases bands appear in the 830-840 cm^{-1} and 720-740 cm^{-1} regions.

The undistorted PF_6^- ion has O_h symmetry, and six normal modes of vibration. In a non-cubic lattice, the symmetry will definitely be lower than O_h due to lack of symmetry elements; in a cubic lattice the symmetry will probably be O_h, but not necessarily so. Slight anion asymmetry may occur which would not affect the crystal lattice. Silver, potassium, rubidium and

caesium fluophosphates have all been shown to possess cubic structures (Kemmitt et al 1963 b), and all these give strong absorptions in the 830-840 cm^{-1} region, with much weaker absorptions around 720-740 cm^{-1}, in all except potassium (Peacock & Sharp 1959; Sharp & Sharpe 1956). The strong absorption was assigned to the V_3 vibrational mode. Woodward and Anderson (1956) measured the Raman spectrum of potassium fluophosphate, and assigned the observed band at 741 cm^{-1} to the V_1 mode. This is the totally symmetric stretching mode of the ion, and is infra-red inactive. Thus it is possible that the 720-740 cm^{-1} bands observed are the V_1 modes in the PF_6^- anion of the salts studied, rendered slightly infra-red active by lowering of the O_h symmetry. In the nitrosonium salt, the bands at 834 cm^{-1} and 740 cm^{-1} are equally strong, and it could be that the PF_6^- anion has been rendered sufficiently asymmetric by the nitrosonium ion, that the V_1 mode is now strongly infra-red active.

The radii of the various cations are:-

	A^o
K^+	1.33
Rb^+	1.48
Ca^+	1.69
Ag^+	1.26
NO^+	1.40 (effective)

It appears that, from the infra-red data, in potassium hexafluophosphate the cation size is such that the O_h symmetry of the anion is undistorted, whereas in the other instances, anion distortion and asymmetry occurs in varying degrees. It might be expected that the extent of asymmetry in the anion, measurable by the relative intensities of the V_1 and V_3 modes, would be dependent on cation radius. However the nitrosonium salt is the only one in which large anion distortion occurs and its effective radius lies between radius values for the other cations; it may be that the shape of the nitrosonium ion is responsible for the extremely large distortion which occurs.

$NO.SO_3F$

This salt is isomorphous with potassium fluosulphate, and both these salts are isostructural with the nitrosonium and potassium fluoborates. This is again due to the non close packed structure of these salts, permitting nitrosonium-potassium replacement without structural change. In both these instances the structure of the anion is tetrahedral or distorted tetrahedral, and the lattice interstices in those structures are much larger than in the hexafluo-metal nitrosonium salts.

As would be expected for isomorphous salts, the infra-red spectrum of the fluosulphate ion is the same for the nitrosonium salt, as for the potassium salt (Sharp 1957). The early preparations of nitrosonium fluosulphate gave two bands in the nitrosonium region, but the lower one, in the 2280 cm^{-1} region was assigned to residual nitrosonium pyrosulphate from the reaction between this, and bromine trifluoride.

$\underline{(NO)_2SnF_6}$

This salt is not isomorphous with the potassium analogue; the presence of a single band in the nitrosonium ion region, at 2342 cm^{-1}, indicates the presence of only one type of lattice site for the nitrosonium ion.

The solid is very hygroscopic, but reacts sufficiently slowly with rigorously dried nujol to obtain infra-red data on the SnF_6^{2-} anion. The value of 547 cm^{-1} is in good agreement with the literature value of 552 cm^{-1} for potassium fluostannate (Peacock & Sharp 1959).

$\underline{NO.AsF_6}$

Like all the other hexafluo-metal salts studied, $NO.AsF_6$ was non-isomorphous with its potassium analogue.

It gave a single infra-red absorption assignable to nitrosonium ion, and the absorption at 700 cm^{-1} assignable to the V_3 mode of the fluoarsenate anion, is the same as that obtained by Peacock & Sharp (1959) for the potassium salt.

NO.HSO4

The literature data on nitrosyl hydrogen sulphate gives the nitrosonium ion a Raman frequency of 2340 cm^{-1} (Gerding & Houtgraaf 1953), although Angus & Leckie (1935) reported a value of 2311 cm^{-1} for the solid salt; in sulphuric acid, they reported values of 2330-2338 cm^{-1} depending on the concentration of water in the sulphuric acid.

On heating, decomposition occurs:-

$$NO.HSO4 \longrightarrow (NO)_2S_2O_7$$

and, as explained in a later chapter, attempts to prepare $(NO)_2SO_4$ have been unsuccessful.

NO.UF_6 and NO.MoF_6

These compounds were obtained as white solids by the gas phase interaction of uranium or molybdenum hexafluorides with nitric oxide (Geichmann et al 1962)

$$MF_6 + NO \longrightarrow NO.MF_6 \qquad (M = U, Mo)$$

The same workers found that no corresponding reaction occurred with tungsten hexfluoride, and that

nitrous oxide reacted with none of these metal fluorides. Also, reactions of the type

$$NOF + MF_5 \longrightarrow NO.MF_6 \qquad (M = U, Mo)$$

gave identical products, and again no reaction occurred with tungsten. Seel & Birnkraut (1962) used the reagent $NOF\,(HF)_3$ to prepare compounds of the formula, $NO.MoF_6$, $NO.UF_6$ and $WF_6.NOF$. The first two are almost definitely identical with the compounds of Geichmann et al (1962). A compound of the same formula as the last mentioned was prepared by Geichmann et al (1963) by the reaction

$$NOF + WF_6 \longrightarrow NO.WF_7$$

The presence of bands at 2330 cm^{-1} and 620 cm^{-1} was assigned respectively to the nitrosonium cation and the heptafluotungstate anion, and it would appear that this is identical with Seel & Birnkraut's $WF_6.NOF$.

Geichmann et al (1963) also prepared the compound nitrosonium heptafluotungstate by the reaction

$$NO_2F + WF_6 \longrightarrow NO_2.WF_7$$

and the nitronium and nitrosonium salts of the hepta-fluo-molybdate and uranate were obtained by analogous reactions. These were all identified and characterised on the basis of their infra-red spectra.

The same workers also found that the reaction between nitrosyl chloride and either molybdenum or uranium hexafluorides, gave respectively $NO.MoF_6$ or $NO.UF_6$. They suggested that this reaction proceeded through an unstable (MoF_6Cl^-) anion which readily dissociated. Again, tungsten hexafluoride did not react.

It is surprising that the attempts to form nitrosonium hexafluotungstate were unsuccessful. The WF_6^- anion is quite well characterised (Sharpe 1960). An explanation of this would probably require a knowledge of the electron affinities MF_6/MF_6^- (where M = Mo,W,U); it may be that the value of this couple for tungsten is considerably less than for molybdenum or uranium.

Other nitronium and nitrosonium salts have been prepared by gas phase interaction but they have not yet been characterised (Robinson & Westland 1956). They are the hexafluoiridates $(NO)_2IrF_6$ and $(NO_2)_2IrF_6$, obtained thus:-

$$2NO + IrF_6 \longrightarrow (NO)_2IrF_6$$

$$2NO_2 + IrF_6 \longrightarrow (NO_2)_2IrF_6$$

These presumably contain iridium (IV) which is well characterised. On heating $(NO)_2IrF_6$ and $(NO_2)_2IrF_6$ give, respectively, $(NO)_2IrF_5$ and $(NO_2)_2IrF_5$, whose structures are unknown.

Geichmann et al (1962, 1963) make no mention of the thermal stability of the nitrosonium metal hexafluorides, but report that several of the hexafluorides do tend to dissociate, though not to lower complex metal fluorides.

$NO.BiCl_4$

This was one of the first metal chloride : nitrosyl chloride adducts to be prepared,(Rheinboldt & Wasserfuhr 1927) by direct interaction of bismuth trichloride with nitrosyl chloride to give a yellow-orange powder. This is very unstable to heat

$$NO \cdot BiCl_4 \longrightarrow BiCl_3 + NOCl$$

The orange colour suggests that some anion-cation interaction may occur in a case such as this, since $BiCl_3$ is colourless. As mentioned in the introduction, in the absence of other chromophoric species colour in nitrosonium ion systems will be due to charge transfer mechanisms of the type

$$NO^+ \quad X^- \longleftrightarrow \dot{N}O \quad \dot{X}$$

and the possibility of a reaction such as this being

appreciable is, in this particular instance, supported by the observation that $NO.BiCl_4$ dissociates very readily so that considerable anion-cation interaction must occur.

$\underline{(NO)_2PdCl_4}$

This compound was first reported by Partington & Whynnes (1949), who prepared it by reaction of palladous chloride with nitrosyl chloride at 100°C; the reaction time was 5 hours. In the present work it was found that palladous chloride and liquid nitrosyl chloride reacted almost instantaneously to give $PdCl_2.2NOCl_{//}$, a bright red compound. An infra-red band at 2330 cm^{-1} established the presence of free nitrosonium ion, and in the absence of bands characteristic of Metal ⟵Nitrosonium ion bonding, the compounds can be formulated $[NO^+]_2\,[PdCl_4^{2-}]$, containing palladium (II). Complexes of the general formula $M_2\,PdCl_4$ (M = alkali metal ion) have been reported in the literature (Sidgwick 1950), and the colours range from yellow to brown, so in this case it is likely that the colour in $(NO)_2PdCl_4$ arises mainly from d-d transitions in the palladium ion.

Reaction of palladium metal with nitrosyl chloride gives $PdCl_2.2NO$ (Partington & Whynnes 1949) and this may contain palladium ⟵ nitrosonium bonds. This type of reaction is unusual, in that the solvolysis reactions involving nitrosyl chloride usually yields nitrosonium salts and not nitrosonium covalent complexes; though gas phase reactions involving nitrosyl chloride do yield the latter (Addison & Johnson 1962).

$NO.ClO_4$

This compound has been shown to be isomorphous with potassium perchlorate (Klinkenberg 1937); the presence of the nitrosonium ion has been confirmed by the presence of a Raman band at 2313 cm^{-1} (Gerding & Houtgraaf). It can be prepared by the solution of dinitrogen trioxide in perchloric acid; as explained in the introduction, the dinitrogen trioxide will yield nitrosonium ion on solution and nitrosonium perchlorate can be precipitated. It has also been prepared by bubbling nitric oxide into an aqueous sulphuric acid/ perchloric acid mixture (Cruse et al 1949).

It is very hygroscopic, and thermally unstable, decomposing below 100° without melting:-

$$2NO.ClO_4 \longrightarrow N_2O_4 + 3O_2 + Cl_2$$

Like the other nitrosonium salts which are isomorphous with their potassium analogues, nitrosonium perchlorate contains a tetrahedral anion; this, again, gives lattice interstices large enough to allow nitrosonium-potassium substitution without structural change.

$(NO).(NO_2)S_3O_{10}$ and $(NO)_2S_2O_7$

Both these compounds are products of nitrogen oxide/sulphur oxide reactions. The nature of these reactions will be more fully dealt with in a later chapter. The structure $(NO).(NO_2)S_3O_{10}$ was assigned on the basis of Raman data, which will be fully covered later.

The compound nitrosonium pyrosulphate appears to contain two nitrosonium ion lattice sites per unit cell, since the infra-red spectrum shows a strong shoulder at 2294 cm^{-1} as well as the main band at 2278 cm^{-1}. Although the structure of the anion is probably based on linked SO_4 tetrahedra, the salt is not

isomorphous with potassium pyrosulphate.

$NO.MnCl_3$

This compound was obtained initially by the passage of nitrosyl chloride over manganous chloride at 260° (Gall & Mengdehl 1927); this seems rather surprising in view of the thermal instability of the compound. Gall & Mengdehl reported a yellow powder; the present work gave, on reaction of manganous chloride and liquid nitrosyl chloride, a golden product. Infra-red examination showed a band at 2271 cm^{-1} and thus this compound could be formulated $NO^{+}MnCl_3^{-}$.

Originally, Asmussen (1939), on the basis of magnetic susceptibility data and thermal stability observations, assigned this compound the structure $[MnNO]^{3+}Cl^{-}_3$. In this case magnetic data are not conclusive since the manganese (II) ion is itself paramagnetic, and the compound was found, also, to be paramagnetic.

The pyridinium salt $[C_5H_5NH]^{+}[MnCl_3]^{-}$ has been prepared (Taylor 1934) and this recrystallises from water as $[C_5H_5NH]^{+}[MnCl_3H_2O]^{-}$, so it is possible that the anion is monomeric; in the absence of single crystal crystallographic data no definite conclusions can be made about the structure of the anion.

The value obtained from the Mn-Cl stretching frequency of 268 cm^{-1} in $NO.MnCl_3$ agrees quite well with the value of 282 cm^{-1} for this mode in the tetrachloromanganite $MnCl_4^{2-}$ anion(9.91). If the $MnCl_3^-$ anion were octahedral, the manganese-chlorine stretching frequency would be less than if it were tetrahedral; hence the infra-red data suggests an octahedral structure but this cannot be regarded as conclusive.

The visible spectrum of the $MnCl_4^{2-}$ anion shows bands in the 445 and 430 mμ regions, (Gill & Nyholm 1959), and the reflectance spectrum of $NO.MnCl_3$ shows a weak band centred about 450 mμ, which may indicate the presence of linked tetrahedral $MnCl_4^{2-}$ units. Compounds which formally contain the MnF_3^- anion are known (Sharpe 1960) though these are in fact perovskites; no fluomanganites or manganate nitrosyl complexes have been reported, so $NO.MnCl_3$ was reacted with bromine trifluoride to see if any nitrosonium fluo-manganese compound could be formed. The only product was manganese trifluoride MnF_3; the nitrosonium chloro-manganite presumably dissociates in bromine trifluoride, manganese trifluoride results and is precipitated out. It has been noted previously that

nitrosonium or nitronium fluo-metal salts are not formed when the metallic 'base' or fluoride is unsoluble in bromine trifluoride. (Woolf & Emeleus 1950).

$NO.CuCl_2$

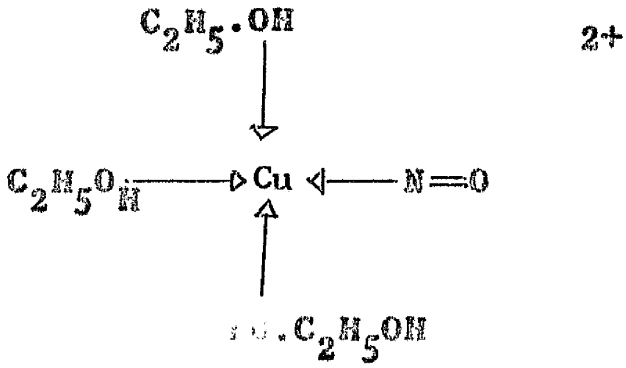
Gall & Mengdehl (1927) reacted cuprous chloride and nitrosyl chloride and obtained a product which they formulated $Cu_2Cl_2.2NOCl$; a similar product was obtained from the reaction between nitric oxide and cupric chloride (Manchot 1910). The latter worker observed that ethanolic cupric solutions, on passage of nitric oxide, became very deep blue or violet. The nitric oxide copper mole ratio was established as being less than 1:1, and by electrolysis experiments it was shown that the nitric oxide was associated with the cation (Manchot 1914).

Asmussen (1939) studied the magnetic behaviour of the compound, and, on the basis of its apparent paramagnetism, formulated it as $[CuNO^{2+}][Cl^-]_2$, assuming the complex ion $[CuNO^{2+}]$ to be paramagnetic due to unpaired electrons on both the copper and nitric oxide groups. However, Burg and MacKenzie (1952)

showed that the freshly prepared compound was diamagnetic. Paramagnetism only came about on standing.

Partington & Whynnes (1948) repeated Gall & Mengdehl's work, and found also that the adduct CuCl.NOCl was obtainable by reacting either copper metal or copper oxide with nitrosyl chloride; no structural observations were made.

Griffith et al (1958 b) studied the infra-red spectra of the compounds $Cu(C_2H_5OH)_3NO\ .Cl_2$ and $Cu(C_2H_5OH)_3NO\ .Br_2$ in ethanolic solution; strong bands in the 1850 cm^{-1} region in each instance indicated that a $Cu^+ \leftarrow NO^+$ linkage was present and the cation would thus be:-

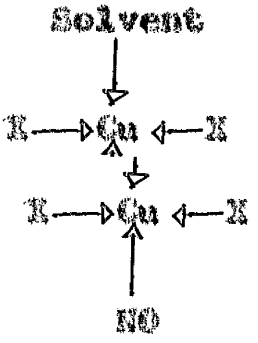


The diamagnetism of the solutions confirmed a $Cu^+ \leftarrow NO^+$ linkage, since cuprous ion has d^{10} configuration and is diamagnetic.

Fraser (1960, 1961) and Fraser & Dasent (1960) have carried out several studies dealing with cupric

halide/nitric oxide equilibria in various solvents. By studying the cupric chloride and bromide systems with nitric oxide in ethanolic solution, Fraser & Basent concluded that with cupric chloride/ethanol chloride, and that in cupric bromide, both neutral cupric bromide and the ionic species $CuBr^+$ absorbed.

A structure for the complex was postulated:-.



X = halogen

and this was assumed to dissociate, to account for the conductivity of these solutions. However, the previous explanation (Griffith et al 1958) seems more probable, since solvation of the copper ion by ethanol molecules seems a more feasible structure than that in the diagram above.

Fraser (1960) also reported the formation of a postulated cupric fluoride/nitric oxide complex in tert-butanol; the deep violet colour of this complex was suggested as being due to $N_2O_2^+$ ion.

From methanol/carbon tetrachloride/cupric halide/nitric oxide systems, the isolation of solids corresponding to the formulas, $CuBr_2.NO$ and $CuCl_2.NO$, has been reported (Mercer & Fraser 1963). These are black solids and give infra-red bands at 1848 cm^{-1} and 1854 cm^{-1} respectively, which definitely classifies them as containing a Cu ◁—NO^+ linkages. These data are not consistent with the present work; in the present work reaction of cuprous chloride with liquid nitrosyl chloride gave, very rapidly, a black solid partially soluble in the excess solvent. On removal of solvent, an ochre-coloured product remained which corresponded to the formula $CuCl_2.NO$; the freshly prepared compound was diamagnetic, confirming the observation of Burg & MacKenzie (1952), and the band at 2271 cm^{-1} in the infra-red spectrum definitely signified the existence of free nitrosonium ion.

It is possible that the black product in nitrosyl chloride solution was a solvate of the compound $NO.CuCl_2$, and that the black $CuBr_2.NO$ and $CuCl_2.NO$ of Mercer & Fraser (1963) are in fact solvates, possibly containing methanol as the ligand. Alternatively it

is possible that the ionic $NO^+.CuCl_2^-$ does exist in a different form in solution, and that equilibria of the type

$$NO^+.CuCl_2^- \rightleftharpoons NO^+ \leftarrow CuCl_2$$

exist, and the form in which it is isolated, is dependent upon the mode of preparation. The nature of the solid $NO^+ \leftarrow CuCl_2$ species could then be either entirely covalent or $[Cu \leftarrow NO^+]^{2+}.2Cl^-$.

The value obtained for the Cu-Cl stretching frequency of 245 cm^{-1} is slightly lower than the values reported by Clark & Dunn (1964) for Cu(II)-Cl frequencies in $[CuCl_4]^{2-}$ salts. This would be expected, since metal-ligand bond frequencies are very sensitive to the oxidation state of the metal.

The structure of the $[CuCl_2]^-$ anion is not known; since it contains Cu(I) which has a d^{10} configuration, no information can be obtained from reflectant spectroscopic data.

$\underline{NO.HgCl_3}$

Gall & Mengdehl (1927) prepared this by the interaction of mercuric chloride and nitrosyl chloride, to yield a red-brown solid. It dissociates very readily.

Asmussen (1939) obtained magnetic susceptibility data on this compound and from these data, and its known thermal instability, postulated it as being a molecular addition compound. Lewis and Sowerby (1957) studied the rate of chloride ion exchange between the compound and liquid nitrosyl chloride, and found evidence for anionic species of the type $HgCl_3^-$, which, it was suggested, were polymeric. The present work confirmed the presence of ionic species; the infra-red absorption band at 2268 cm^{-1} is in the characteristic region for nitrosonium ion.

No evidence was obtained to prove or disprove the presence of polymeric anionic species. The far infra-red spectrum gave a single absorption at 261 cm^{-1}, due to an Hg-Cl stretching mode.

$NO.AlCl_4$

Reaction of anhydrous aluminium chloride and liquid nitrosyl chloride gives a white solid, soluble in nitrosyl chloride. This confirmed the observations of Gerding & Houtgraaf (1953) who obtained a similar product; Partington & Whynnes (1948) had obtained a lemon-yellow product melting with decomposition. This has been explained as being due to the existence of

two allotropic forms, the metastable one being the latter (Addison & Lewis 1955).

Gerding & Houtgraaf (1953) obtained a Raman displacement of 2236 cm^{-1} for the compound, and the compound $AlCl_3.NaCl$, gave identical low frequency Raman displacements to $NO.AlCl_4$, confirming the presence of $AlCl_4^-$ in the latter.

Because the value of 2236 cm^{-1} obtained for the stretching mode of the nitrosonium ion was much lower than that of the same ion in nitrosyl hydrogen sulphate, Gerding & Houtgraaf postulated that anion-cation polarisation occurred in $NO.AlCl_4$ to lengthen the N-O bond in the cation and thus lower the frequency. They postulated an equilibrium:-

$$NO^+.AlCl_4^- \longleftrightarrow AlCl_3.....Cl.....NO$$

and the value for the nitrosonium ion stretching mode would depend on which form, the ionic or molecular, was predominant. This type of polarisation probably does occur and will be discussed later in this chapter.

Partington & Whynnes (1948) also prepared adducts closely related to $NO.AlCl_4$, viz:- $GaCl_3.NOCl$, $InCl_3.NOCl$ and $TlCl_3.NOCl$. These have not been examined to verify the presence of free

nitrosonium ion, but it is most probable that they are of the same structure as the aluminium adduct. Seel & Sauer (1957) examined their behaviour under nitric oxide pressure in sulphur dioxide solution and observed the purple colouration typical of $N_2O_2^+$ iom; thus it can be assumed that the above adducts are ionic compounds.

$NO)_2PtCl_6$

Klinkenberg (1938) has shown this to be isomorphous with potassium chloroplatinate; the present work confirmed this (table 2), and obtained the nitrosonium ion frequency as being consistent with the formulation $(NO^+)_2$ $(PtCl_6^{2-})$. The compound is red, and fairly stable compared to many other nitrosonium salts.

The data on the $PtCl_6^{2-}$ anion (table 3) show it to be unaffected by the change in the cation; this would be expected for isomorphous salts of different cations.

$NO.FeCl_4$

This was first obtained by Rheinboldt & Wasserfuhr (1927) by direct interaction of ferric chloride and nitrosyl chloride. The behaviour of

the compound in nitrosyl chloride solution was studied by Burg & MacKenzie (1952), who concluded that it ionised in solution into NO^+ and $FeCl_4^-$, the former probably solvating to $[NOCl.NO]^+$ species.

The present work confirmed the existence of the compound in the solid state as $NO^+FeCl_4^-$. The reflectance spectrum gave a broad absorption centred about 530 mμ; this agrees with other data on chloroferrates by Friedmann (1952), who observed a 532 mμ band in solid potassium chloroferrate and in an $FeCl_3$/12M HCl mixture, and Gill (1961) who studied tetraethylammonium chloroferrate and observed strong bands at 533 mμ and 685 mμ. Neither authors assigned these bands.

The data on the $FeCl_4^-$ anion agrees quite well with that for the tetraethylammonium salt (table 3); the literature data on the chloroferrate and -ferrite shows the marked dependence on the oxidation state of the metal atom.

Seel & Birnkraut (1962) reacted iron with nitrosyl hydrogen fluoride $NOF(HF)_3$ and obtained an adduct $NOF.FeF_3$, which may be $NO^+FeF_4^-$; if this is so, it is the first reported example of FeF_4^- ion.

In an attempt to prepare Seel & Birnkraut's compound, $NO.FeCl_4$ was dissolved in bromine trifluoride, and the excess solvent removed. The only product was ferric fluoride.

$(NO)_2SnCl_6$

This has been shown to be isomorphous with potassium chlorostannate (Klinkenberg 1938) and the present work confirmed this. Since the two salts are isomorphous anion-cation polarisation is likely to be small, if present at all.

$(NO)_2SnCl_6$ is a pale yellow solid; it is much more stable in moist air than its fluo-analogue $(NO)_2SnF_6$. Asmussen (1939) observed its thermal stability and from this and magnetic susceptibility data formulated it as an ionic compound $(NO^+)_2(SnCl_6^{2-})$.

The far infra-red data on the $SnCl_6^{2-}$ anion (table 3) shows a good agreement between the potassium and nitrosonium salts as would be expected, for isomorphous compounds. The 310 cm^{-1} band is presumably the ν_3 mode.

$NO.SbCl_6$

This compound, and the previous one, both prepared by reaction of nitrosyl chloride with the high valency metal chloride, in carbon tetrachloride

solution (Rheinboldt & Wasserfuhr 1927). $NO.SbCl_6$ is pale yellow, and stable to heat. Like the chlorostannate couple, it is more stable to hydrolysis than its fluo analogue $NO.SbF_6$. The far infra-red shows an absorption at 345 cm^{-1} (table 3) presumably due to the V_3 mode.

$NO.ZnCl_3$

This compound was prepared by Asmussen (1939); like $HgCl_2.NOCl$, it was found to be thermally unstable, and the two compounds gave similar magnetic properties which led Asmussen to formulate it as a molecular addition compound. However, the present work shows it to be a nitrosonium salt $NO^+ZnCl_3^-$, although the colour suggests that anion-cation polarisation may occur. Apart from the charge transfer system

$$NO^+ \quad Cl^- \longleftrightarrow NO^\cdot \quad Cl^\cdot$$

no other chromophore is present.

The far infra-red data on the anion agrees quite well with other far infra-red data on Zn(II)-Cl band frequencies (table 4). As in $NO.HgCl_3$, it has been suggested that the $ZnCl_3^-$ anion is polymeric (Lewis & Sowerby 1957) but no evidence for this has been obtained.

$(NO)_2TiCl_6$

Like the chloro-stannate and antimonate, $(NO)_2TiCl_6$ is obtained by the reaction of nitrosyl chloride and a high valency metal chloride, in this case titanium tetrachloride, in nitrosyl chloride (Rheinboldt & Wasserfuhr 1927). It is very readily hydrolysed, leaving a residue of titanium dioxide, even in moist air. It sublimes very readily, even at room temperature.

It is not isomorphous with its potassium analogue; all this suggests that a high degree of anion-cation polarisation occurs, similar to that postulated by Gerding & Houtgraaf for $NO.AlCl_4$.

The far infra-red band at 478 cm^{-1} is due to the $TiCl_6^{2-}$ anion but due to the possible distortion of the anion, it is not possible to assign this band.

Discussion.

Table 1 shows that the range of the NO^+ absorption extends over nearly 230 cm^{-1}; Seel (1950) and Gerding & Houtgraaf (1953) explained this in terms of partial covalent character:-

$$NO^+ \cdot MCl_n^- \longleftrightarrow NO\ldots Cl\ldots MCl^-_{n-1}$$

The partial formation of an N-Cl bond like this would

lengthen the N-O bond and so lower the vibrational frequency of the N-O stretching mode. This explanation was adequate to describe the bond frequency differences in compounds such as $NO.HSO_4$, $NO.AlCl_4$ and $NO.SbCl_6$. In the latter two, partial cation polarisation would occur due to partial N-Cl bond formation; this would not occur with nitrosyl hydrogen sulphate to the same extent.

Table 1 shows that this explanation is not adequate. The compounds $NO.BF_4$, $NO.SO_3F$, $NO.ClO_4$, $(NO)_2PtCl_6$ and $(NO)_2SnCl_6$ are all isomorphous with their potassium analogues. This makes it unlikely that anion-cation polarisation occurs in these instances since such polarisation would be very likely to distort the lattice. Also, since in all cases except the perchlorate, the infra-red spectra of the anions of the nitrosonium salt and the corresponding potassium salt are identical, it seems most unlikely that any polarisation occurs in these compounds, yet their nitrosonium ion stretching frequencies range from 2387 cm^{-1} ($NO.BF_4$) to 2191 cm^{-1} $(NO)_2SnCl_6$.

No clear trends in nitrosonium ion frequencies are evident from Table 1 ; in general, it appears that salts of fluo-acids give higher frequencies than salts of oxy-acids, which in turn, give higher frequencies that salts of chloro-acids. Also, the observations mentioned before about the greater tendency towards hydrolysis of $(NO)_2SnF_6$ and $NOSbF_6$ than their chloro-analogues, suggests that in the latter instances, the nitrosonium ion is less susceptible to nucleophilic attack by water molecules; this could be due to polarisation occurring to lower the electropositive nature of the cation, but this would probably distort the lattice, and with $(NO)_2SnCl_6$, this has been shown not to be the case.

Obviously the factors influencing the nitrosonium ion stretching frequency are very complex, and two interactions may be responsible:-

1. Cation - Halogen interaction.
2. Cation - Central metal atom interaction.

In cases involving hexa-co-ordinate anions, the latter interaction is unlikely to be very important, since the central metal atom is well shielded by halogens; this will probably be the case

with four co-ordinate anions also. Cation-Metal atom interaction may well be important in some of the lower chloro-metal salts. Shielding by halogens is unlikely to be so marked and, if polymeric anions do occur in any of these instances as has been suggested (Lewis & Sowerby 1957), the compounds could well have a layer lattice structure as has been shown to exist in $(NH_4).HgCl_3$ (Hermsen 1938), in which both types of interaction are possible.

There is little correlation between the stability of the compound, either towards hydrolysis or towards dissociation, and its nitrosonium ion absorption frequency. The fluoro-salts showed little tendency towards dissociation, and the majority of the chloro-salts tend to dissociate fairly readily, irrespective of nitrosonium ion frequency. Many of the fluoro-salts with high nitrosonium ion frequencies hydrolyse extremely readily, but in several cases hydrolysis may involve the anion, which forms oxide or oxyfluoride species.

All of the chloro-adducts except $(NO)_2PtCl_6$, $(NO)_2SnCl_6$ and $NO.SbCl_6$ gave additional bands at 1800 cm^{-1}, and these were originally assigned to metal ⟵ NO^+ bonding. However, the bands were not present in fresh samples and increased in intensity with time; dissociation, giving nitrosyl chloride, with subsequent infra-red absorption by nitrosyl chloride seems a more probable explanation:-

$$NO.MCl_n \longrightarrow M.Cl_{n-1} + NOCl$$

though isomeric change may occur.

The x-ray data (table 2) shows that the only nitrosonium salts of hexa co-ordinate anions isomorphous with their potassium analogues, were two of the chloro-salts. None of the fluo-salts exhibited isomorphism. Complex halides generally have structures based on close-packing of halide ions and cations. The radii of the fluoride ion and potassium ion are equal (1.33A); that of the nitrosonium ion is 1.40 when spherical, hence a fluoride ion lattice is unable to accommodate nitrosonium ions without distortion. The radius of the chloride ion is 1.81A and this is large enough to accommodate the nitrosonium ion in a chloride-ion lattice, and enable

it to achieve spherical symmetry by rotation. Nitrosonium fluoborate, fluosulphate and perchlorate, isomorphous with their potassium analogues, do not have close-packed structures.

The far infra-red spectra of the anions studied (tables 3 → 5), do show the presence of metal-halogen bonds, but give no information about the structure of the anions. If an anion MX_3^- is planar it has D_{3h} symmetry; if dimeric, with an Al_2Cl_6 type structure, the symmetry is V_h. In the former case, three of the four vibrational modes would be infra-red active, in the latter case eight of the eighteen modes would be infra-red active. In practice, several of the infra-red active modes of the anion of V_h symmetry are deformation modes of such low frequency that they came below 200 cm^{-1}, the lower frequency limit of the investigation. In addition, decomposition in the nujol mulls complicated the spectra, and resolution of the instrument was often poor. Hence only the major infra-red bands could be obtained.

In the chloroplatinates, the bands observed may be the V_3(300 cm^{-1}) and V_4(265 cm^{-1}) modes; these are the only infra-red active modes of an anion of

of the $PtCl_6^{2-}$ type (O_h symmetry group) and the V_3 vibration is usually the highest (Nakamoto 1963). Hence the bands observed in the chlorostannates and in nitrosonium chloroantimonate are likely to be the V_3 modes also.

The 370 cm^{-1} band in nitrosonium chloroferrate will be the V_3 mode of the tetrahedral, or distorted tetrahedral $FeCl_4^-$ anion.

Since the structures of the anions $CuCl_2^-$, $ZnCl_3^-$, $HgCl_3^-$ and $MnCl_3^-$ are unknown, it is not possible to assign the observed bands for these compounds.

EXPERIMENTAL

Nitrosyl chloride was prepared as described in the experimental section of the following chapter; bromine trifluoride was prepared by bubbling chlorine trifluoride through bromine at c. 0°C, until the dark colour of the bromine had been replaced by the straw-colour of pure bromine trifluoride. The reaction usually took 1 - 1½ hours for 20 - 30 mls. bromine. It was found that reaction proceeded most smoothly if the initial temperature of reaction was 15° - 20°C, i.e. about room temperature. The reaction was allowed to proceed at this temperature for 10 - 15 minutes, thereafter being cooled to 0°C.

All the nitrosonium fluo-salts were prepared by Woolf's method (Woolf 1950) and the potassium fluo-salts by that of Woolf & Emeleus (1949).

$(NO)_2GeF_6$

Nitrosyl chloride, in about 20% - 50% excess was transferred by vacuum-distillation into a silica reaction flask containing germanium dioxide. The flask was removed from the vacuum line and bromine trifluoride added dropwise through a copper funnel, with the reaction mixture cooled to - 184°C (liquid oxygen temperature).

When an excess of bromine trifluoride had been added the reaction was allowed to come up to room temperature. After the reaction had stopped, the excess nitrosyl chloride and bromine trifluoride was removed by distillation in vacuo at 80° - 90°. A white solid remained.

Analysis: Found N:10.9% $(NO)_2GeF_6$ requires N:11.4%.

$NO.VF_6$

This was prepared as above, using vanadium pentoxide instead of germanium dioxide. A white solid was the reaction product.

Analysis: Found N:6.2% $NO.VF_6$ requires N:7.0%.

The low value in this case is probably due to the rapidity with which $NO.VF_6$ hydrolysed.

$NO.BF_4$

Bromine trifluoride was reacted with boric oxide and nitrosyl chloride, as described above. The white product remaining was analysed.

Found N:11.6% $NO.BF_4$ requires N:12.0%.

$NO.SbF_6$

Bromine trifluoride was reacted with antimony pentoxide and nitrosyl chloride; after removal of excess solvent a white solid remained.

Found N:5.0% $NO.SbF_6$ requires N:5.2%.

$NO.PF_6$

Bromine trifluoride was reacted with phosphorous pentoxide and nitrosyl chloride; this reaction was violent, inflaming at times. On removal of excess solvent a white product remained.

Analysis: Found N:7.8% $NO.PF_6$ requires N:8.0%.

$NO.SO_3F$

Nitrosonium pyrosulphate $(NO)_2S_2O_7$ was dissolved in bromine trifluoride. On evaporation of excess solvent, a white solid remained.

Analysis: Found N:10.5% $NO.SO_3F$ requires N:10.8%.

$(NO)_2SnF_6$

Stannous chloride was dissolved in bromine trifluoride and excess solvent removed in vacuo at 200°C to give stannic fluoride. This was reacted with nitrosyl chloride and bromine trifluoride to give, on evaporation of excess solvent, a white solid.

Analysis: Found N:9.3% $(NO)_2SnF_6$ requires N:9.6%.

$NO.AsF_6$

Bromine trifluoride was reacted with arsenious oxide and nitrosyl chloride. After removal of excess solvent, a white solid remained.

Analysis: Found N:6.1% $NO.AsF_6$ requires N:6.4%.

$NO.BiCl_4$

This was prepared by the method of Rheinboldt & Wasserfuhr (1927). Nitrosyl chloride was transferred by vacuum distillation into a Carius tube containing dry bismuth trichloride. The tube was sealed in vacuo and the mixture raised to room temperature. On careful removal of solvent, a yellow-orange powder remained. If too high a vacuum was applied, dissociation occurred yielding bismuth trichloride.

Analysis: N:3.6% Cl: 36.2% $NO.BiCl_4$ requires N:3.7% Cl: 37.0%.

$(NO)_2S_2O_7$

Nitrogen dioxide, whose preparation is described in the experimental section of the next chapter, and sulphur dioxide, were separately vacuum distilled into Carius tube, at - 184°C. After sealing the tube, the reaction was allowed to proceed at room temperature for 24 hours (Hart-Jones et al 1929). A pink-violet solid resulted which became white on evacuation. The colour was presumably due to $N_2O_2^+$ ion.

Analysis: Found N:10.0% $(NO)_2S_2O_7$ requires N:10.2%.

$NO.MnCl_3$

Nitrosyl chloride was transferred by vacuum distillation into a Carius tube containing anhydrous manganous chloride, prepared by heating $MnCl_2.6H_2O$ at 150^o - 200^o for several hours. The tube was sealed and the mixture raised to room temperature; on evaporation of excess solvent, a golden solid remained.

Analysis:

Found N:7.1% Cl:55.0% $NO.MnCl_3$ requires N:7.3% Cl:55.1%.

$NO.CuCl_2$

Nitrosyl chloride was transferred by vacuum distillation into a Carius tube containing cuprous chloride, and the tube sealed off. On raising to room temperature a black solid and solution resulted, which on evaporation of excess solvent gave an ochre solid.

Analysis: N:8.3% Cl:42.6% $NO.CuCl_2$ requires N:8.5% Cl:43.1%.

$NO.HgCl_3$

Nitrosyl chloride was transferred by vacuum distillation into a Carius tube containing mercuric chloride, and the tube sealed. After reaction at room temperature, excess solvent was carefully removed to

leave a red-brown solid. If too high a vacuum was applied during this stage, all the nitrosyl chloride was removed leaving mercuric chloride.

Analysis:

N:3.8% Cl:30.1% $NO.HgCl_3$ requires N:4.2% Cl:31.6%.

$\underline{NO.AlCl_4}$

Nitrosyl chloride was condensed on to anhydrous aluminium chloride in a Carius tube, and the tube sealed. After reaction at room temperature the excess solvent was removed under vacuum, leaving a white solid.

Analysis:

N:6.7% Cl:70.6% $NO.AlCl_4$ requires N:7.0% Cl:71.3%.

$\underline{(NO)_2PtCl_6}$

Nitrosyl chloride was condensed on to chloroplatinic acid $H_2PtCl_6.H_2O$ in a Carius tube, and the tube sealed. After reaction at room temperature the excess solvent was removed and a yellow-brown solid remained.

Analysis:

N:5.9% Cl:45.6% $(NO)_2PtCl_6$ requires N:6.0% Cl:45.5%.

$(NO)_2PdCl_4$

Nitrosyl chloride was condensed on to palladous chloride in a Carius tube and the tube sealed. After reaction at room temperature, the excess solvent was removed, leaving a red-brown solid.

Analysis:

N:9.0% Cl:46.3% $(NO)_2PdCl_4$ requires N:9.1% Cl:46.1%.

$NO.FeCl_4$

Nitrosyl chloride was condensed on to anhydrous ferric chloride in a Carius tube, and the tube sealed. After reaction at room temperature, removal of excess solvent left a yellow-ochre solid.

Analysis:

N:6.1% Cl:62.0% $NO.FeCl_4$ requires N:6.2% Cl:62.3%.

$(NO)_2SnCl_6$

Nitrosyl chloride, stannic chloride and carbon tetrachloride were separately distilled into a reaction flask (100 ml.) in vacuo. Dry air was admitted and the reaction allowed to come up to room temperature, when a pale yellow solid rapidly separated out. Excess nitrosyl chloride and carbon tetrachloride were removed in vacuo and the pale yellow solid remained.

Analysis:

N:6.8% Cl:54.0% $(NO)_2SnCl_6$ requires N:7.2% Cl:54.4%.

$NO.SbCl_6$

This was prepared in a similar manner to the above, using antimony pentachloride instead of stannic chloride. The yellow solid product obtained was analysed.

Analysis:

N:3.7% Cl:58.2% $NO.SbCl_6$ requires N:3.8% Cl:58.3%.

$NO.ZnCl_3$

Nitrosyl chloride was condensed on to zinc chloride in a Carius tube, in vacuo, and the tube sealed. After reaction of room temperature, removal of excess solvent left a pale yellow product which tended to dissociate on application of a vacuum.

Analysis:

N:6.6% Cl:52.0% $NO.ZnCl_3$ requires N:6.9% Cl:52.7%.

$(NO)_2TiCl_6$

Nitrosyl chloride, titanium tetrachloride and carbon tetrachloride were transferred separately by vacuum distillation into a reaction flask. Dry air was admitted and the reaction mixture raised to room temperature, when a pale yellow solid separated out. Excess carbon tetrachloride and nitrosyl chloride were

removed in vacuo.

Analysis:

N:8.2% Cl:65.4% $(NO)_2TiCl_6$ requires N:8.7% Cl:66.3%.

Preparation of potassium salts.

K_2GeF_6

Potassium chloride and germanium dioxide were mixed in a 2:1 mole ratio, and placed in a silica reaction flask. Bromine trifluoride was added dropwise until an excess was present; the reaction took place at room temperature and the excess solvent was removed in vacuo at 200°C. A white solid remained.

Analysis:

Ge:27.4% K_2GeF_6 requires Ge:27.6%.

$K.VF_6$

Potassium chloride and vanadium trichloride in a 1:1 mole ratio (for preparation, see chapter on vanadium group metals) were reacted in the same manner as above. A white solid was obtained.

Analysis: V as V_2O_5:24.8% $K.VF_6$ requires V:25.0%.

$K.SbF_6$

Potassium chloride and antimony pentoxide in a 2:1 mole ratio were reacted in the same manner as above

A white solid product was obtained.

Analysis:

Sb:43.9% $K.SbF_6$ requires Sb:44.4%.

$K.SO_3F$

Potassium persulphate $K_2S_2O_8$ was dissolved in bromine trifluoride. On evaporation of excess solvent as above, a white solid remained.

Analysis:

S%:23.2% $K.SO_3F$ requires S:23.2%.

$K.PF_6$

Potassium chloride and phosphorous pentoxide were reacted in a 2:1 mole ratio with bromine trifluoride, and the excess solvent removed, as above. A white solid remained.

Analysis:

F = 60.9% KPF_6 requires F = 61.9%.

K_2SnF_6

Stannic fluoride was prepared by reacting stannous chloride with bromine trifluoride and removing the excess solvent at 200°C. This was then mixed with potassium chloride (SnF_4:KCl = 1:2 mole ratio) and treated with bromine trifluoride as above. After

removal of excess solvent at 200°C a white solid remained.

Analysis:

Sn:38.1% K_2SnF_6 requires Sn:38.3%.

$\underline{K.AsF_6}$

Potassium chloride and arsenous oxide were mixed in a 2:1 ratio and the same procedure followed as with K_2GeF_6 etc. A white solid was obtained.

Analysis:

As:33.0% $KAsF_6$ requires AS:32.9%.

$\underline{K_2SnCl_6}$

A solution of hydrated stannic chloride was made up in concentrated hydrochloric acid, potassium chloride added, and then chlorine bubbled through with constant stirring. The solution soon turned yellow, and pale yellow crystals started to be precipitated. The reaction was stopped after 40 - 50 minutes and the super-natant liquor allowed to settle, before most of it was decanted. The residue was filtered by suction, washed with glacial acetic acid, then ethanol and finally ether. The bulk of the ether was removed by rapid suction, and the remainder dried in vacuo. The

product was a pale yellow solid.

Analysis:

Cl:52.0% K_2SnCl_6 requires Cl:51.9%.

X-ray photographs were taken in Lindemann glass capillaries with Cu-K_α radiation; the photographs were measured visually, but calculation of $Sin^2\theta$ values and indexing of powder lines were carried out on a Ferranti Sirius Computer, using programmes developed by Russell (1963).

Infra-red spectra were measured as mulls in florube grease using calcium fluoride windows. It was found that even the most reactive nitrosonium salts were fairly stable in florube mulls. The nitrosonium salts tended to decompose very readily in nujol, even when rigorously dried, and also in hexachlorobutadiene.

All preparations of mulls had to be carried out in the dry box. Spectra were measured on a Grubb Parsons DB1 spectrophotometer, using sodium chloride optics. All the values of nitrosonium ion frequencies tabulated (table 1) were calibrated against a polystyrene spectrum, using the 3.42μ and 6.24μ bands as references.

TABLE 1 NITROSONIUM ION STRETCHING FREQUENCIES

	COMPOUND	$\nu(NO^+)$ in cm^{-1}	
	$(NO)_2GeF_6$	2391s.	shoulder at 2336.
	$NO.VF_6$	2391s.	shoulder at 2328.
i	$NO.BF_4$	2387s.	2341 (e,f).
	$NO.SbF_6$	2385b.	shoulder at 2342.
	$NO.PF_6$	2379s.	
i	$NO.SO_3F$	2377b.	
	$(NO)_2SnF_6$	2342s.	
	$NO.AsF_6$	2340s.	
	$NO.HSO_4$	2340 (a): 2311 (b)	Both Raman spectra.
	$NO.UF_6$	2333	measured as (c) sublimed films
	$NO.MoF_6$	2331	
	$NO.BiCl_4$	2331b.	
	$(NO)_2PdCl_4$	2330s.	
i	$NO.ClO_4$	2313 (d)	Raman spectra.
	$(NO).(NO_2)_2.(S_3O_{10})$	2308, 2277 (d)	Raman spectra.
	$(NO)_2S_2O_7$	2278s.	shoulder at 2294.
	$NO.MnCl_3$	2271b.	
	$NO.CuCl_2$	2271b.	
	$NO.HgCl_3$	2268b	
	$NO.AlCl_4$	2242s.	shoulder at 2370; 2236 (a) Raman spectra.
i	$(NO)_2PtCl_6$	2201s.	

TABLE 1 contd.

$NO.SbCl_6$	2189s.
$NO.ZnCl_3$	2187b.
$NO)_2TiCl_6$	2165b.

All data obtained from the present work, except

(a) Gerding & Houtgraaf 1953.

(b) Angus & Leckie 1935.

(c) Geichmann et al 1962.

(d) Gerding & Eriks 1952.

(e) Sprague et al 1960.

(f) Evans et al 1964.

The letter i - indicates nitrosonium compounds found to be isomorphous with their potassium analogues.

TABLE 2 X-RAY DATA

ORTHORHOMBIC STRUCTURES

	Unit Cell Dimensions (Å)				Unit Cell Volumes
	a	b	c		(Å^3)
$NO.BF_4$	8.88	5.64	7.03	1)	352.2
	8.79	5.66	7.10		
$K.BF_4$	7.83	5.67	7.35	2)	326.3
	7.85	5.68	7.37		
$NO.SO_3F$	8.71	6.20	7.31		403.9
$K.SO_3F$	8.55	5.94	7.34	3)	372.8
	8.56	5.95	7.33		

CUBIC STRUCTURES

	a (Å)	
$(NO)_2SnCl_6$	10.24	
K_2SnCl_6	10.14	2)
	10.14	
$(NO)_2PtCl_6$	11.27	
K_2PtCl_6	11.20	2)
	11.18	

All present work except -

1) Klinkenberg 1937.

2) Wykoff, 'Crystal Structures'.

3) Sharp 1957.

TABLE 3 V_3 MODE FREQUENCIES IN NITROSONIUM SALTS OF CHLORO-ANIONS

COMPOUND	V (cm^{-1})	
$(NO)_2SnCl_6$	310	
K_2SnCl_6	312	
$(NO)_2PtCl_6$	267,300	lower values are probably the V_4 modes
K_2PtCl_6	265,300	
$NO.SbCl_6$	345	
$NO.FeCl_4$	370 a)	
$(C_2H_5)_4N.FeCl_4$	378 a)	
$(C_2H_5)_4N\ {}_2FeCl_4$	282	

TABLE 4 METAL-CHLORINE STRETCHING FREQUENCIES IN NITROSONIUM SALTS OF CHLORO-ANIONS

$NO.CuCl_2$	245	
$(C_2H_5)_4N\ _2CuCl_4$	247m; 268s; 289sh.	a)
CS_2CuCl_4	256m; 288sh.	a)
$NO.ZnCl_3$	270	
$(C_2H_5)_4N\ _2ZnCl_4$	273s; 281m.	a)
CS_2ZnCl_4	285m; 292s.	a)
$NO.MnCl_3$	268	a)
$(C_2H_5)_4N\ _2MnCl_4$	282	
$NO.HgCl_3$	261	
$(NO)_2TiCl_6$	478	

s - strong m - medium sh - shoulder

All present work except -

a) Clark & Dunn 1964.

TABLE 5 FLUORO-ACID SALTS: INFRA-RED DATA ON ANIONS

COMPOUND	BANDS (cm^{-1})	
$NO.BF_4$	770w, 1061s, 1075s, 1305w, 1790w.	a), b)
$K.BF_4$	771w, 1032w, 1058s, 1072s, 1302w, 1784w.	
$NO.SO_3F$	1300s, 1282s, 1076s, 731s.	c)
$K.SO_3F$	1299s, 1277s, 1073s, 732s.	
$NO.PF_6$	834s, 740s.	
$K.PF_6$	845 [a], 741 [e] (Raman active)	
$Rb.PF_6$	845s, 802w, 740-720w.	f)
$Cs.PF_6$	843s, 802w, 740-720w.	f)
$Ag.PF_6$	830-840s, 740w.	f)
$(NO)_2SnF_6$	547	
K_2SnF_6	552	d)
$NO.SbF_6$	660	
$K.SbF_6$	660	d)

References

a) Cote & Thompson 1951.

b) Edwards et al 1955.

c) Sharp 1957.

d) Peacock & Sharp 1959.

e) Woodward & Anderson 1956.

f) Sharp & Sharpe 1956.

CHAPTER II

SOLVENT PROPERTIES OF NITROSYL CHLORIDE AND DINITROGEN TETROXIDE

THE NITRATO - LIGAND

The majority of the reactions described in the following chapters are effectively solvolysis reactions of metal and non-metal chlorides, in either nitrosyl chloride or dinitrogen tetroxide solution; in some cases metal bromide - nitrosyl bromide reactions have been attempted.

In the case of a metal chloride/nitrosyl chloride reaction, it is possible to write the following general equation

$$MCln + NOCl \longrightarrow MCln \cdot NOCl \qquad (1$$

i,e. an adduct is formed which may react either with another molecule of nitrosyl chloride or the metal chloride; in the former case an adduct of the general formula MCln. 2NOCl is formed, in the latter case 2MCln.NOCl. When a variety of products are formed, it is normally possible to manipulate the reaction to give a predominant yield of one product by varying the relative concentrations of the metal chloride and nitrosyl chloride used.

With dinitrogen tetroxide solvolyses, the situation is more complex due to the possibility of more reactions occurring and hence a greater variety of products being formed. The initial reaction step is of the type:-

$$MCl_n + n\,N_2O_4 \longrightarrow M(NO_3)_n + n\,NOCl \qquad 2$$

The nitrosyl chloride may then react with the metal chloride to yield adducts such as MCl_n NOCl as in reaction 1.

It is possible that the nitrate $M(NO_3)_n$ may undergo several types of decomposition or dissociation, viz:-

$$M(NO_3)_n \longrightarrow MO_2(NO_3)_{n-2} + N_2O_4 \qquad 3$$

In this case the oxidation number of M increases by two. Also the dissociation

$$M(NO_3)_n \longrightarrow MO(NO_3)_{n-2} + N_2O_4 + {}^1/_2\,O_2 \qquad 4$$

can occur, in which the oxidation state of M is unchanged.

Reaction 3 is obviously favoured when the original oxidation state of the metal is not the highest possible; also, the M - O bonds formed are usually multiple bonds and have considerable bond strength. Since no such bonding exists in the pure nitrates, this makes the formation of the oxynitrates in reactions 3 and 4 thermodynamically favourable. Whether a particular metal

nitrate will undergo reaction 3 or 4 will depend on the relative stabilities of the oxidation states formed, the most stable one being favoured. The nitrate and oxynitrates formed in reactions 2 , 3 , and 4 are all potentially capable of forming adducts with dinitrogen tetroxide, thus the variety of products which can be formed is potentially very large. Particular cases in which this situation appears to occur will be dealt with individually in later chapters.

Reaction 2 illustrates the production of nitrosyl chloride in a dinitrogen tetroxide system. As the concentration of dinitrogen tetroxide falls, the concentration of nitrosyl chloride increases. It has been shown that, with uranium, the solvolytic behaviour of nitrosyl chloride/dinitrogen tetroxide mixtures is markedly dependent on the ratio of the components (Addison & Hodge 1961a). These workers found that dinitrogen tetroxide will not react with uranium except in the presence of nitrosyl chloride, but that up to a nitrosyl chloride percentage concentration of 85%, the only product was $UO_2(NO_3)_2.N_2O_4$. At nitrosyl chloride concentrations above this $UO_2Cl_2.NOCl$ was formed.

In metal chloride/dinitrogen tetroxide systems, the amount of nitrosyl chloride formed is dependent on the concentration of the metal chloride; this is evident from equation 1 . Hence the composition of the nitrosyl chloride/dinitrogen tetroxide mixture at any stage of such a reaction is dependent on the original metal chloride: dinitrogen tetroxide ratio, and thus the products formed may also be dependent on this ratio.

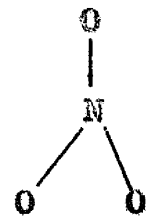
These are, in all cases, reactions in dinitrogen tetroxide or nitrosyl chloride solution, in which the reactant species invariably appear to be ions, in the former case, NO^+ and NO_3^-, in the latter NO^+ and Cl^-. In the gas phase reactions are markedly different since the reactive species are either NO_2 radicals or NOCl molecules. To illustrate the difference in gas and liquid phase reactions, the reaction

$$Ni(CO)_4 + 2NOCl \longrightarrow NiCl_2 + 4CO + 2NO$$

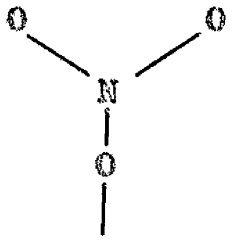
occurs in the liquid phase, while the same components give dichloronitrosylnickel (I) in the gas phase (Addison & Johnson 1962); nickel carbonyl reacts in the liquid phase with dinitrogen tetroxide to give to $Ni(NO_3)_2.2N_2O_4$, whereas in the gas phase the product is nickel dinitrite $Ni(NO_2)_2$. (Addison & Sutton 1963). The subject of nitrogen dioxide free radical reactions in this context has been reviewed by Addison (1962).

When nitrate groups are involved in metal systems they can exist either as free nitrate ions, or as bonded nitrato - ligands. Straub et al (1962) have prepared dimethyl sulphoxide complexes of manganese, cobalt and nickel which contain the anions $M(NO_3)_4^{2-}$ M = Mn, Co, Ni ; cationic complexes containing the nitrato - ligand have been postulated in Sb([illegible] $As(NO_3)_4^{+}$ and $Sb(NO_3)_4^{+}$ cations respectively (Dehnicke 1964). The first workers to examine the infrared spectra of nitrates were Miller & Wilkins (1952), who were attempting to characterise the band frequencies of the nitrate ion. They amassed a considerable amount of spectroscopic data but did not make assignments of any bands, though they noted that a broad absorption in the 1300 - 1400 cm^{-1} region seemed to be characteristic of nitrate ion.

The infrared spectra of nitrates have been more fully examined by Gatehouse et al (1957), Addison & Gatehouse (1960) and Katzin (1962). The symmetry properties of the free nitrate ion and the co-ordinated nitrato - group are set out below:-



nitrate ion
Symmetry D_{3h}



nitrato - group
Symmetry C_{2v}

By co-ordination of one oxygen atom, the symmetry of the nitrato - group is lowered, relative to the free ion.

The nitrate ion has 4 fundamental frequencies; these have been assigned and the frequency ranges obtained (Gatehouse et al 1957; Addison & Gatehouse 1960).

NITRATE ION

TYPE		RAMAN	INFRARED	RANGE	ASSIGNMENT
A	(V_1)	a	ia	c.1050 cm^{-1}	N-O symmetric stretch
A	(V_2)	ia	a	c. 830 cm^{-1}	NO_2 deformation
E	(V_3)	a	a	c.1390 cm^{-1}	NO_2 asymmetric stretch
E	(V_4)	a	a	c.720 cm^{-1}	Planar Rock

a - active ia - inactiv e.

The same workers have carried out a similar analysis for the co-ordinated nitrato-group

NITRATO-GROUP

TYPE		RAMAN	INFRARED	RANGE (cm^{-1})	ASSIGNMENT
A_1	(V_3)			c. 739	NO_2 banding
A_1	(V_1)	all active		1290-1253	NO_2 symmetric stretch
A_1	(V_2)			1034-970	NO stretch
B_2	(V_6)			800-781	non-planar rock
B_1	(V_4)			1531-1481	NO_2 asymm. stretch
B_1	(V_5)			c.713	planar rock

Effectively, co-ordination of the nitrate ion, and hence conversion into nitrato-ligand, has split the V_3 vibration of NO_3^- ion into the V_1 and V_4 modes of the nitrato-group, the symmetric and asymmetric stretching modes of the $-NO_2$ group; also, the V_4 vibration of the NO_3^- ion has been split into the V_3 and V_5 modes of the nitrato-group, which gives a much smaller splitting than that due to (V_4 - V_1). The lowering of the symmetry by co-ordination has rendered the symmetric N-O stretching mode, infrared inactive in the nitrate ion, active in the co-ordinated ligand as the V_2 vibration.

From the preceding tables it is observed that for both free nitrate ion and the co-ordinated nitrato-group, bands occur in the 700-750 cm^{-1} region. The nitrato-group shows the V_6 band at a quite significantly lower range (781-800 cm^{-1}) than the V_2 nitrate mode (830 cm^{-1}). In both instances, bands occur in the 1050 cm^{-1} region but the V_1 mode of the nitrate ion is only Raman active, hence presence of a band in this region of the infrared spectrum is a good indication of co-ordinated nitrato-groups.

Finally, the V_3 band of the nitrate ion at 1390 cm^{-1} is split into two widely separate bands in approximately the 1500 cm^{-1} and 1270 cm^{-1} regions in the co-ordinated nitrato-group and this is used as the primary evidence for the presence of co-ordinated nitrato-ligands.

The amount of the (V_4-V_1) splitting in the co-ordinated ligand is dependent on the extent of deformation caused by co-ordination. If metal-ligand bonding is weak, ligand deformation will be small and the subsequent splitting will also be small. Thus it is possible to use the magnitude of this splitting as a roughly quantitative guide to the covalency of a nitrato-complex. Katzin (1962) has studied the spectra of several nitrates in tritutylphosphate solution and has found that even with obviously ionic nitrates, some splitting of the V_3 vibration of the nitrate

ion occurs, but this was of a magnitude (less than 65 cm^{-1}) that could be explained by electrical asymmetry. When the splitting was greater than 125 cm^{-1}, it was stated that significant covalency occurred, and the higher this splitting, the greater the extent of covalency.

Several compounds are known in which a (V_4-V_1) splitting greater than 300 cm^{-1} occurs, which can be taken to indicate high covalency in the compound. Also, cases have been postulated in which the nitrato-group behaves as a bidentate ligand, in trinitratoniobium oxide (Field & Hardy 1963a) and anhydrous chromium trinitrate (Addison & Chapman 1964).

Dinitrogen pentoxide is known to exist in the solid state as nitronium nitrate NO_2^+ NO_3^- (Teranishi & Decius 1953, 1954) and in nitric acid dissociates into the same ions. (Millen 1950b). It would thus be expected to be a good reagent for introducing the nitrate or nitrato-group into metallic compounds and it has been employed for this purpose (Schmeisser & Lutzow 1953; Schmeisser & Elisher 1957; Ferraro et al. 1955; Gibson et al. 1960; Field & Hardy 1962, 1963a,b; Addison & Chapman 1964; Bagnall et al 1964). In general, it is a much more useful reagent for introduction of nitrate groups, than is dinitrogen tetroxide, since the side reactions are, much

fewer. The initial reaction stage in the solvolysis of a metal halide by dinitrogen pentoxide is

$$MCln + \frac{n}{2}N_2O_5 \longrightarrow M(NO_3)_n + nNO_2Cl$$

The nitryl chloride thus formed does not tend to form adducts with the metal chloride in the same manner as nitrosyl chloride. Also the tendency to form adducts with the metal nitrate is much smaller with dinitrogen pentoxide than dinitrogen tetroxide, though the adduct $Th(NO_3)_4 \cdot 2N_2O_5$ is stable up to over 100°C (Ferraro et al 1955), and in this case is more stable than the dinitrogen tetroxide adduct.

The adducts of the types $M(NO_3)_n \cdot N_2O_4$, and $MCln \cdot NOCl$ are analogous; the former refers to the dinitrogen tetroxide solvent system, the latter to the nitrosyl chloride system.

However, the two systems are not entirely analogous. For instance, Zinc Chloride forms the adduct $ZnCl_2 \cdot NOCl$, which is structurally $NO^+ \cdot ZnCl_3^-$. With dinitrogen tetroxide, zinc nitrate forms the adduct $Zn(NO_3)_2 \cdot 2N_2O_4$; no 1 : 1 adduct in this system is known. Moreover, although this adduct dissociates in solution, thus

$$Zn(NO_3)_2 \cdot 2N_2O_4 \longrightarrow (NO^+)_2 + Zn(NO_3)_4^{2-}$$

(Addison & Hodge, 1954b)

the dinitrogen tetroxide is believed to be present merely as a 'lattice compound' in the solid state (Addison et al 1958). Several other instances occur where analogy is not complete, and it is thus not possible to draw too many structural conclusions on various adducts on the basis of analogy with other solvent systems.

With many of the solid products obtained in the reactions described in later chapters, infrared examination in vigorously dried nujol mulls was not invariably accurate due to the decomposition and in many cases it was necessary to determine bands due to the original compounds by observing the time dependence of the spectroscopic bands. Field & Hardy (1963,b) have also noted this; they reported that nitrate-compounds tended to nitrate nujol and postulated a radical mechanism breakdown:-

$$MO.NO_2 \longrightarrow \dot{M}O + \dot{N}O_2$$

which Addison (1962) had reported. Florube was a much less reactive mulling agent but its range was rather limited (4000 - 1350 cm^{-1}).

The preparations of nitrosyl chloride, nitrosyl bromide and dinitrogen tetroxide are described in the experimental section of this chapter. Although nitric oxide does come into a different category than these reagents, it is also described here for convenience.

EXPERIMENTAL.

As mentioned previously in this chapter, it is highly important that nitrosyl chloride used in solvolysis reactions should be free of dinitrogen tetroxide, and vice versa.

The preparations of nitrosyl chloride, nitrosyl bromide and dinitrogen tetroxide are described below.

NITROSYL CHLORIDE.

Nitrosonium hydrogen sulphate was obtained by reaction of sulphur dioxide and nitric acid for 4 - 6 hours at c.0°C.

$$HNO_3 + SO_2 \longrightarrow NO.HSO_4$$

The yellow solid was rapidly filtered by suction; it was then mixed intimately with dried sodium chloride. During this stage the reaction was frozen down to prevent too much loss of nitrosyl chloride due to the following reaction:-

$$NO.HSO_4 + NaCl \longrightarrow NOCl + NaHSO_4$$

The nitrosyl chloride evolved was condensed in a trap at -78°C; at this temperature any hydrogen chloride impurities are not condensed out.

The gas phase spectrum of the nitrosyl chloride gave bands as follows:-

1818 m, 17998, 1740 m, 738, 746, 758 (s). (cm^{-1})

The first three of these bands are due to the -N=O bond stretching mode and the split bands centred about 746 cm^{-1} are due to the N-Cl stretching vibration.

NITROSYL BROMIDE

The analogous reaction to the above for the preparation of nitrosyl bromide was unsatisfactory; the $NO.HSO_4$ / NaBr had to be heated to 50° - 60° to get steady nitrosyl bromide evolution, and the following reactions occurred.

$$NO.HSO4 + NaBr \longrightarrow NO.Br + NaHSO_4$$

$$2NO.Br \longrightarrow 2NO + Br_2$$

$$2NO + O_2 \longrightarrow 2NO_2 \rightleftharpoons N_2O_4$$

The nitrosyl bromide dissociates quite easily, and the nitric oxide formed reacted with atmospheric oxygen as shown, to give nitrogen dioxide impurity, which condenses out as dinitrogen tetroxide with nitrosyl bromide. As will be enlarged upon later, the presence of dinitrogen tetroxide impurities had a considerable influence on the vanadium bromides / nitrosyl bromide systems.

The most satisfactory method was the reaction in vacuo of nitrosonium pyrosulphate and sodium bromide; the reaction proceeded quite steadily at 110°-130°. The volatile products were condensed out at 198°.

$$(NO)_2S_2O_7 + 2NaBr \longrightarrow Na_2S_2O_7 + 2NOBr$$

Obviously, at 110°-130°, nitrosyl bromide dissociates markedly but in this system no atmospheric oxidation can occur, and the product appear to recombine at low temperatures.

$$2NOBr \rightleftharpoons 2NO + Br_2$$

The infrared spectrum gave strong bands at 1768 cm^{-1} and 1760 cm^{-1} due to the -N=O bond stretching frequencies, and a weak band at 1880 cm^{-1} due to nitric oxide.

DINITROGEN TETROXIDE.

Lead nitrate was heated strongly, and the dinitrogen tetroxide condensed out in acetone/CO_2.

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

The infrared spectrum shows strong bands at 1698 cm^{-1} and 1208 cm^{-1} due to asymmetric and symmetric stretching modes of the bent nitrogen dioxide; also a weak combinational band at 2896 cm^{-1} is present.

Hence, if dinitrogen tetroxide is present as an impurity in nitrosyl halides, it will be easily distinguishable from the gas phase infrared spectrum, and for this reason, gas spectra were run on every batch of nitrosyl halides and dinitrogen tetroxide prepared.

NITRIC OXIDE

This was prepared as in Inorganic Syntheses, Volume 2, p.126; the reduction of sodium nitrite by acidified ferrous sulphate solution in the absence of oxygen. Acidified ferrous sulphate was added dropwise to sodium nitrite solution, the system being previously swept out with nitrogen, the gas was evolved steadily, passed through concentrated sodium hydroxide to remove traces of nitrogen dioxide, then passed through phosphorus pentoxide tubes to remove water vapour, and condensed in a trap cooled down in liquid oxygen (at - 184°C). The nitric oxide separated out as a very pale blue solid. Any formation of nitrogen dioxide due to leakages in the system, was very easy to follow because of the brown coloration produced.

In all the above cases, the product was redistilled in vacuo over phosphorus pentoxide at least twice, before reactions, to remove residual moisture.

CHAPTER III

REACTIONS OF NITROGEN OXIDES AND NITROSYL CHLORIDE WITH LEWIS ACIDS OF GROUPS IIIB, IVB, AND VB.

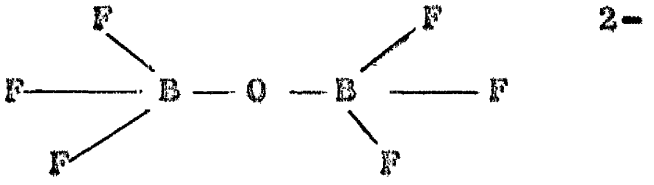
BORON TRIFLUORIDE/NITROGEN OXIDES

Nitrogen oxides are known to react with Lewis acids such as boron trifluoride (Bachmann et al 1955; Sprague et al 1960; Kuhn & Olah 1961; Olah & Tolgyesi 1961; Evans et al 1964). These products can be formulated as adducts of the reactants, and because of their ability to act as nitrating and nitrosylating agents, they were formulated as salts containing nitronium or nitrosonium ions and complex anions.

Bachmann, from a study of the nitrating properties of the $BF_3.N_2O_4$ complex, formulated it as $NO_2^+ \cdot BF_3.NO_2^-$; the composition of the product was independent of the reaction phase, i.e. gas, liquid or solute phase. Later, Kuhn & Olah (1961) observed that the same complex had nitrosylating properties, and from Raman investigations, suggested that the structure was an equilibrium, viz:-

$$NO_2^+ \quad BF_3.NO_2^- \qquad\qquad NO^+ \quad BF_3.NO_3^-$$

Sprague and his colleagues (1960) suggested, from infrared and x-ray observations, that the reaction product was $NO^+ . NO_2^+ . (BF_3)_2O^{2-}$; the anion in the latter case was postulated to have the structure



and so for x-ray purposes would be very similar to the tetrafluoborate ion.

Finally, Evans et al (1964) showed that the reaction could be explained without recourse to postulating complex anion formation. They studied the reaction of boron trifluoride with dinitrogen trioxide, tetroxide and pentoxide, and their conclusions can be summarized thus:-

$$N_2O_3/BF_3 \longrightarrow NO.BF_4 + \text{borates} \qquad 1$$

$$N_2O_4/BF_3 \longrightarrow NO.BF_4 + NO_2.BF_4 + \text{borates} \qquad 2$$

$$N_2O_5/BF_3 \longrightarrow NO_2.BF_4 + \text{borates} \qquad 3$$

In all these cases the main products were nitrosonium or nitronium fluoborate with only small quantities of borate species being formed. Reaction 2 explains why the $BF_3.N_2O_4$ adduct possesses both nitrating and nitrosylating properties.

Other reactions involving boron halides which have been studied are:-

1. Boron trichloride/Nitrosyl chloride.

Olah & Tolgyesi (1961) reported the formation of a solid complex when these components react at -50°C; the solid dissociates at room temperature. The infrared spectrum shows a band at 2123 cm^{-1} and so the compound can be regarded as $NO^+ . BCl_4^-$

2. Boron trifluoride/Nitrosyl chloride.

These components react in liquid hydrogen chloride solution to give a product of composition $BF_3.NOCl$, which is orange, and sublimes with dissociation at 25°C (Waddington & Klanberg 1960). The infrared spectrum shows a band at 2335 cm^{-1} which indicates free nitrosonium ion, hence Waddington & Klanberg formulate the adduct as $NO^+ . BF_3Cl^-$. However, Kemmitt et al (1963a), on the basis of infrared and nuclear resonance studies on haloborates, conclude that there is no definite evidence for the existence of mixed haloborate anions.

Since the nitrosonium ion is colorless, the orange colour of this complex implies that significant anion - cation charge transfer must occur.

Comparing these last two adducts with nitrosonium fluoborate, the order of thermal stability is:-

$NO.BF_4$ > $No.BF_3Cl$ > $No.BCl_4$

as would be expected. The fall in the nitrosonium ion vibrational frequency suggests that anion-cation polarisation depends on the number of chloride groups present in the anion.

In addition Waddington & Klanberg (1960) report the compound $NO^+ . B(C_2H_5)_3Cl^-$, which gives an abnormally high infrared band at 2480 cm^{-1} which is assigned to the nitrosonium ion, but no mention is made of its stability.

GROUP IV HALIDES/NITROGEN OXIDES

The reactions of silicon and germanium halides have not been studied in the present work; however, Devin & Perrot (1958) demonstrated that $(NO)_2SiCl_6$ and $(NO)_2GeCl_6$ could not be formed by direct interaction of silicon or germanium tetrachloride with nitrosyl chloride. Waddington & Klanberg (1960) confirmed this, attempting to react the components in liquid hydrogen chloride.

Stannic Chloride/Nitric Oxide.

Nitrosyl chloride reacts with stannous chloride to give nitrosonium hexachlorostannate $(NO)_2SnCl_6$. If any intermediates such $(NO)_2SnCl_4$ are formed, they do not exist long enough in the presence of nitrosyl chloride

to be studied. Nitric oxide and stannic chloride were reacted in carbon tetrachloride to see if any such intermediates could be isolated. A white solid was rapidly precipitated giving a very weak absorption in the free nitrosonium ion region but repeated analyses were inconsistent. No other bands in the infrared spectrum were observed. It appears that these reactions are best explained thus:-

$$SnCl_4 + 2NO \longrightarrow SnCl_2 + 2NOCl$$

$$SnCl_4 + 2NOCl \longrightarrow (NO)_2SnCl_6$$

Thus the main product is stannous chloride, with a small quantity of nitrosonium chlorostannate, accounting for the weak NO^+ absorption.

Stannic Chloride/Dinitrogen tetroxide.

This reaction gives at least two products. It was carried out as a possible means of obtaining anhydrous stannic nitrate $Sn(NO_3)_4$. The reaction had already been carried out by Partington & Whynnes (1949), who obtained an adduct which they formulated $SnCl_4 . 2.5\ NO_2$, which was probably a mixture of products.

The present work gave a white solid, insoluble in dinitrogen tetroxide which could not be separated by sublimation. It was highly moisture sensitive, hydrolysing with copious evolution of nitrogen dioxide, indicating

the presence of nitrosonium ion. The infrared spectrum gave a strong band at 2200 cm^{-1}; and bands in the 1250 cm^{-1} and 1600 cm^{-1} regions which could be the V_1 and V_4 modes of a covalently bonded nitrato-group. Other bands were present at 1000 cm^{-1} and 800 cm^{-1}. The product was found to contain chloride so that it could not be a simple nitrato compound. It would appear that the following types of reaction occurred:-

$$SnCl_4 + 4N_2O_4 \longrightarrow Sn(NO_3)_4 + 4NOCl$$

$$SnCl_4 + 2NOCl \longrightarrow (NO)_2SnCl_6$$

$$Sn(NO_3)_4 + N_2O_4 \longrightarrow \text{adducts.}$$

The infrared spectrum definitely indicates covalently bonded nitrato-groups but cannot be regarded as conclusive.

In addition the reaction

$$Sn(NO_3)_4 \longrightarrow SnO(NO_3)_2 + N_2O_4 + {}^1/_2O_2$$

may occur; this type of dissociation is known to occur with titanium tetranitrate (Gutmann 1956). Hence, as pointed out previously, this type of reaction can yield several products. Analysis, together with the above data, suggests primarily a mixture of tetranitratotin and nitrosonium chlorostannate.

GROUP V HALIDES/NITROGEN OXIDES

Previous work in this field has been carried out on adducts of dinitrogen tetroxide with arsenic and antimony pentafluorides (Aynsley et al 1951); phosphorus chlorides and oxychlorides with dinitrogen tetroxide (Klement & Wolf 1955); arsenic and antimony trichlorides with nitrosyl chloride (Lewis & Sowerby 1957; Waddington & Klanberg 1960); and the antimony pentachloride/nitric oxide reaction (Bowen 1954).

The present work involved the partial study of the reactions of phosphorus pentafluoride with nitric oxide and dinitrogen tetroxide.

Phosphorus pentafluoride/nitric oxide.

These react to give a very small yield of a white product which rapidly decomposes with evolution of nitrogen dioxide fumes. No studies were possible on this, but it may be similar to the $BF_3.NO$ and $SO_3.NO$ adducts reported in the litrature; these may be further examples of compounds containing one electron bonds (Bues 1952).

Phosphorus pentafluoride/dinitrogen tetroxide.

These react in the liquid phase very readily at room temperature to give immediate separation of a white solid. This gave a very complicated infrared spectrum

due to decomposition taking place in the Nujol mull. Decomposition even occurred in florube mulls. Measuring spectra as a function of time it was possible to assign the following bands to the mixture of complexes believed to be formed:-

3700w, 2390s, 2360(Sh), 1780w, 1700w, 1120m, 1030s, 840s, 740m, 660m. (all cm^{-1})

This suggests that a mixture of nitrosonium and nitronium species were formed, and the following assignments can be made on this basis:-

3700	-	$(\nu_1 + \nu_3)$ NO_2^+ ion
2390	-	ν_3 NO_2^+ ion
2360	-	ν_1 NO^+ ion
1780	-	not assignable
1700	-	possibly $2\nu_3$ PF_6^-
1120, 1030	-	P - O multiple bond stretching frequencies
840	-	probably ν_3 PF_6^-
740	-	probably ν_1 PF_6^- (strictly infrared inactive)
660	-	ν_2 NO_2^+ ion

Nitronium fluoborate and fluoantimonate have been shown to give spectra agreeing quite well with these assignments (Cook et al. 1960). Values for ν_3 of the nitronium ion vary from 2387 cm^{-1} (Cook et al 1960) in the fluoantimonate.

The existence of the nitronium ion is supported by the weak combinational band at 3700 cm^{-1}. Cook et al (1960) also report a band at 855 cm^{-1} assigned as V_3 of the fluophosphate ion. In addition, Sharp & Sharpe (1956) report that the spectra of the fluophosphates of rubidium, caesium and silver give bands in the 840 cm^{-1} and 720-740 cm^{-1} regions. As stated in a previous chapter, the spectrum of nitrosonium fluophosphate shows bands at 834 cm^{-1} and 740 cm^{-1}. Hence it seems reasonable to assign the two bands at 840 cm^{-1} and 740 cm^{-1} to the V_3 and V_1 modes of the fluophosphate ion. The bands at 1120 cm^{-1} and 1030 cm^{-1} suggest the formation of phosphate entities involving P = O multiple bonding, possibly leading to polyanion formation. It will be seen that this reaction is analogous to the boron trifluoride/dinitrogen tetroxide reaction in that a mixture of nitrosonium and nitronium species are apparently formed.

Hence the behaviour of nitrogen oxides with Lewis Acids bears a strong resemblance to the behaviour of nitrogen oxides in strong acid systems, which is covered in the introductory chapter.

Phosphorus trichloride and oxytrichloride/dinitrogen tetroxide.

Phosphorus trichloride reacted violently with dinitrogen tetroxide at about $0^{o}C$ to give a number of

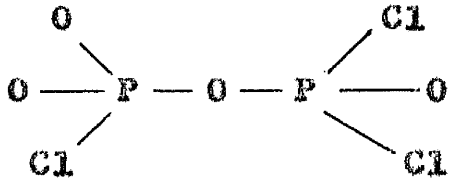
products. One of the volatile products of the reaction was phosphorus oxytrichloride identified by its melting point and boiling point. The solid residue could not be further purified and inconsistent analyses suggested a mixture of products.

Reaction of dinitrogen tetroxide with phosphorus oxychloride yielded one product in the solid residue, analysing as PO_4NCl.

The infrared spectrum showed the following bands:- 3700 vw, 2380 sh, 2250 s, 1600 w, 1050 - 1000 s. (all cm^{-1}). Given the formula $(PO_4NCl)_n$, and assuming phosphorus to be in the +5 oxidation state, a reasonable structure for the above compound incorporating nitrosonium ions cannot be formulated unless nitronium ions exist also. Assuming n = 2, the following formula is possible:-

$$[NO^+] \quad [NO_2^+] \quad [P_2O_5Cl_2^{2-}]$$

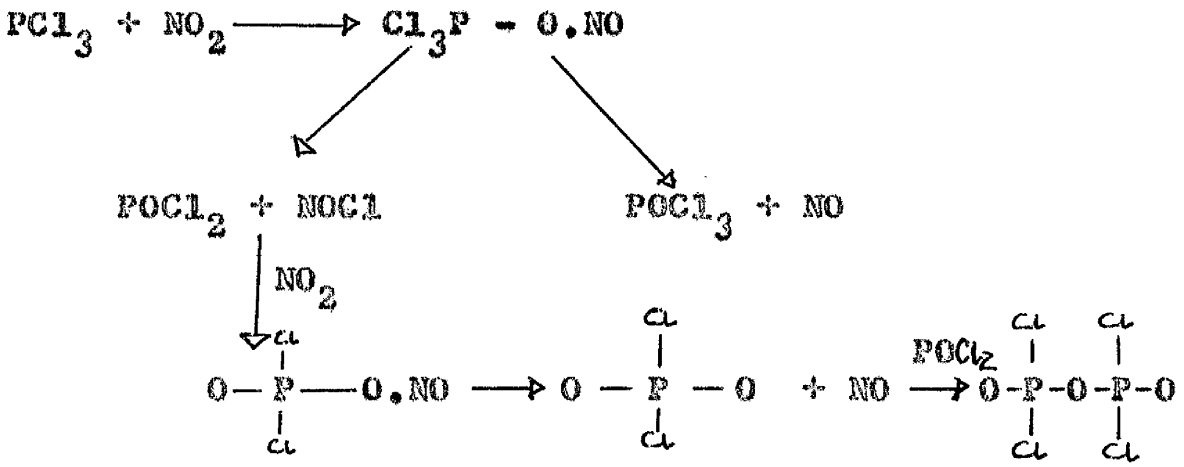
in which the complex anion involved could have the following structure:-



Any structures containing -O.NO or $-O.NO_2$ groups linked to the phosphorus atoms would be easily distinguishable from

the infrared spectrum. The gas phase reaction between phosphorus trichloride and nitrogen dioxide has been studied (Klement & Wolf 1955) and as might be expected the reaction course is slightly different, since nitrogen dioxide radicals are now the reactive species. The same may possibly occur in dinitrogen tetroxide solution, but, as has been observed previously, the reactive species in the liquid phase always appear to be ions.

Klement and Wolf postulate the initial formation of a highly reactive radical intermediate which can dissociate in two ways:-



Reaction of phosphorus oxytrichloride with nitrogen dioxide yields $P_2O_6NCl_2$ (Klement & Wolf 1955), presumably by a similar type of mechanism; no structure is suggested for the species. The above mechanism could operate in dinitrogen tetroxide solution with initial cleavage of N_2O_4 species; or attack could be by nitrate ion,

eliminating chloride ion; with nitrogen dioxide eventually cleaving from the reaction species. This would give largely the same reaction pattern.

Other reactions studied involving phosphorus chlorides were:-

Phosphorus pentachloride/Dinitrogen tetroxide.

This reaction gave a white solid, stable under pressure, but which rapidly dissociated at room temperature and atmospheric pressure.

Phosphorus trichloride or pentachloride/nitrosyl chloride.

Attempts to form PCl_4NO species and to form $NO^+ PCl_6^-$ were not successful; the former reaction gave only phosphorus pentachloride, and no sign of reaction occurred in the latter case.

ARSENIC TRICHLORIDE/NITROSYL CHLORIDE.

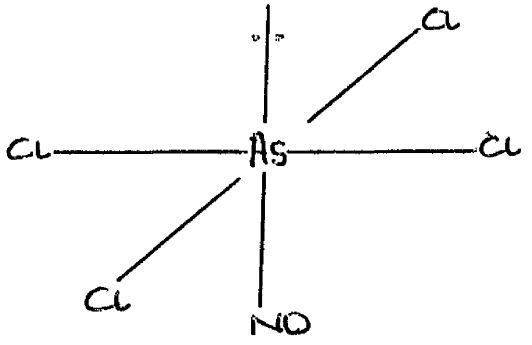
This reaction was found to give two products, a red liquid, $AsCl_4.NO$, and a white solid stable under pressure of nitrosyl chloride but which dissociated at room temperature and atmospheric pressure.

Lewis & Sowerby (1957) studied the arsenic trichloride/nitrosyl chloride equilibrium and found evidence for the formation of a weak complex $AsCl_3.2NOCl$, to which the white solid observed in the present work

may correspond. Waddington & Klanberg (1960) carried out the reaction in liquid hydrogen chloride and observed only the species $AsCl_4.NO$ with no other adduct formation. Their compound $AsCl_4.NO$ was a red liquid, with a strong infrared absorption at 1860 cm^{-1} indicating co-ordinated nitrosonium ion, the present work confirms this.

The gas phase spectrum gave a strong bond at 1852 cm^{-1} in good agreement with Waddington & Klanberg's value. The volatility of the compound (boiling point 60° - 70°) indicates monomeric structure, implying that arsenic is tripositive and penta - co-ordinate.

The structure of this may be based on a hexaco-ordinate arsenic atom, with a pair of electrons occupying one of the positions, viz:-



As yet, there is no proof that the nitrosyl group is bonded to the arsenic atom via the nitrogen atom, or that the As——NO system is linear. This system could possibly be similar to the nitrosyl halides, which are bent molecules.

ARSENIC TRICHLORIDE/DINITROGEN TETROXIDE.

These react rapidly to give a white solid and a little of the compound $AsCl_4.NO$ mentioned above; the solid analysed as $As(NO_3)_3.N_2O_4$.

The postulated reaction scheme follows the normal pattern for this type of reaction.

$$AsCl_3 + 3N_2O_4 \longrightarrow As(NO_3)_3 + 3NOCl$$

$$As(NO_3)_3 + N_2O_4 \longrightarrow As(NO_3)_3.N_2O_4$$

$$AsCl_3 + NOCl \longrightarrow AsCl_4.NO$$

As with the reaction products in similar systems, the compound decomposes in Nujol mulls, and time-dependent spectra were used to assign the following bands to the compound $As(NO_3)_3.N_2O_4$:-

2220m; 1850w; 1613m; 1252m; 1012s; 805s; 750w.

Assuming that the adduct is the nitrosonium salt (NO^+) $(As(NO_3)_4^-)$, the following assignments can be made:-

2220 - $\nu_1(NO^+)$

1850 - $(\nu_2 + \nu_6)$ nitrato - group

1613 - ν_4 nitrato-group

1252 - ν_1 nitrato-group

1012 - ν_2 nitrato-group

805 - ν_6 nitrato-group

750 - ν_3 or ν_5 nitrato group.

The bands assignments are satisfactorily in agreement with the ionic formulation, and the $(V_4 - V_1)$ splitting, in the nitrato-group, of 361 cm^{-1}, indicated a high degree of covalency in the $As(NO_3)_4^-$ anion, on Katzin's criterion (1962).

Attempts to obtain the anhydrous nitrate $As(NO_3)_3$ by heating the adduct were unsuccessful; the only products were arsenic trioxide and nitrogen oxides.

ANTIMONY PENTACHLORIDE/NITRIC OXIDE

This reaction followed initially a similar pattern to the analogous stannic chloride reaction; i.e. reduction occurs:-

$$SbCl_5 + 2NO \longrightarrow SbCl_3 + 2NOCl \qquad 1$$

Unlike stannous chloride, antimony trichloride is soluble in carbon tetrachloride, the reaction medium, and the second reaction is:-

$$SbCl_3 + NOCl \longrightarrow SbCl_4.NO \qquad 2$$

This compound was first prepared by Waddington and Klanberg (1960) who reacted antimony trichloride and nitrosyl chloride in liquid hydrogen chloride; in addition, the compound $(NO)_2\ SbCl_5$ was observed in this system, which was not observed in the present work.

In the present work, also it was found that the following reaction interfered when the antimony pentachloride concentration was too high:-

$$SbCl_5 + NOCl \longrightarrow NO.SbCl_6 \qquad 6$$

However, when low concentrations of antimony pentachloride were used, it was found that practically complete reduction (reaction (1)) occurred, before reaction 3 became significant.

The infrared spectrum of $SbCl_4.NO$ gave a band at 1900 cm^{-1}, agreeing with Waddington & Klanberg's formulation of this as a covalent compound containing -Sb-N=O bonding, though, as in $AsCl_4.NO$, bonding to the central atom could occur via the oxygen atom.

The gas phase reaction of antimony pentachloride and nitric oxide has been carried out, and the product reported to be a yellow crystalline polymer $(SbCl_5)_2NO_n$ (Bowen 1954), but no structural data were given. He reported that when the reaction mixture was cooled to -196°C, a purple coloration appeared which vanished above -110°C. This purple coloration is typical of ions involving one-electron bonds, i.e. of the type $N_2O_2^+$, formed under pressure of nitric oxide by the reaction $NO^+ + NO \rightleftharpoons N_2O_2^+$ (Seel et al 1953; Seel & Sauer 1957).

Thus Bowen's compound is likely to contain nitrosonium ions and may be a mixture of compounds such as $NO.SbCl_6$ and $NO.SbCl_4$.

ANTIMONY PENTACHLORIDE/DINITROGEN TETROXIDE

This reaction is difficult to study for the reasons outlined in the previous chapter, i.e. many competing reactions occur and most of the products are solids and difficult to separate.

Infrared examination showed evidence for formation of nitrosonium and nitronium ions, and covalently bonded nitrato-groups, but no products could be satisfactorily isolated. Heating caused degradation to the pentoxide with evolution of nitrogen oxides, and no products could be sublimed out.

ADDUCTS OF ARSENIC AND ANTIMONY PENTAFLUORIDES.

Arsenic and antimony pentafluorides have been shown to react with nitrogen dioxide (Aynsley et al 1951) to form adducts analysing as $AsF_5.NO_2$ and $SbF_5.NO_2$ but nothing is known of their structures. These appear to be definitely single compounds as $AsF_5.NO_2$ sublimes at 57^oC without decomposition, and nitrosonium and nitronium fluoarsenate sublime at much higher temperatures than this.

Whereas reactions of the type MCl_n/N_2O_4 always seem to involve considerable replacement of chloride by nitrato-groups, this occurs only to a very small extent if at all, with MF_n/N_2O_4 reactions. In general MX_n/N_2O_4 reactions (M=central metal or non-metal atom; X=halogen) can occur in the following ways:-

1. Salt formation

$$MX_n + N_2O_4 \longrightarrow NO.MX_{n+1} + NO_2.MX_{n+1} + MOX \text{ species}$$

2. Adduct formation

$$MX_n + \tfrac{1}{2}N_2O_4 \longrightarrow MX_n.NO_2 \text{ : these could be ionic}$$

3. Substitution Reactions

$$MX_n + nN_2O_4 \longrightarrow M(NO_3)_n + nNO\,X$$

The first two reactions do not involve M-X bond fission and the second would be favoured by a high concentration of NO_2 radicals and thus by gas phase reaction. Fluorides undergo these reactions (1 and 2) preferentially, probably on account of the higher M-F bond strength, compared to the M-Cl bond. Also, it is possible that reactions of type 3 are favoured because of the free energy of formation of nitrosyl chloride compared nitrosyl fluoride.

Considering fluorides, boron trifluoride and phosphorus penta-fluoride came into category 1 , with arsenic and antimony pentafluorides in category 2 .

Both the reaction types involve the fluoride behaving as acceptors; electrostatically the latter two will be the stronger acceptors because of the lower electronegativity of the arsenic and antimony atom, but it is difficult to see how this favours $-NO_2$ co-ordination, rather than fluoride ion co-ordination. Conclusive statements are not possible without a knowledge of the structures of the $AsF_5.NO_2$ and $SbF_5.NO_2$ adducts. Also, it is possible that under exactly identical reaction conditions, all these compounds would react similarly.

NITROGEN OXIDE/SULPHUR OXIDE REACTIONS

These reactions can be considered as coming into the same category as the ones previously discussed, since sulphur dioxide and trioxide can both behave as Lewis acids; sulphur trioxide, in particular, is highly analogous to boron trifluoride and phosphorus pentafluoride:-

$$SO_3 + O^{2-} \longrightarrow SO_4^{2-}$$

$$BF_3 + F^- \longrightarrow BF_4^-$$

$$PF_5 + F^- \longrightarrow PF_6^-$$

Sulphur dioxide also tends to behave similarly but in this case the sulphite species produced are very susceptible to oxidation to give sulphates.

Reactions between sulphur trioxide and nitrogen oxides have been extensively covered by several workers (Goddard et al 1950; Lehmann & Kluge 1951; Gerding & Eriks 1952), and are highly similar to the nitrogen oxide/sulphuric acid systems studied by other workers and discussed in the introductory chapter.

The reaction between sodium nitrite and sulphur trioxide yields on vacuum distillation $N_2O_3 \cdot 3SO_3$; and similar treatment of the potassium nitrate/sulphur trioxide mixture yields $N_2O_5 \cdot 4SO_3$ (Lehmann & Kluge 1951). The latter product dissociates at 60°C to $N_2O_5 \cdot 3SO_3$ and sulphur trioxide; also some $N_2O_4 \cdot 3SO_3$ is formed.

Gerding & Eriks (1952) examined the $N_2O_4 \cdot 3SO_3$ adduct and from the Raman spectrum assigned the structure $(NO^+)(NO_2^+)(S_3O_{10}^{2-})$; bands at 1400 cm^{-1} and 2277 cm^{-1} were assigned to the V_1 and V_3 modes of the nitronium ion, and an absorption at 2308 cm^{-1} was assigned to the nitrosonium ion.

Similarly, the other complexes were assigned the following structures

$N_2O_5 \cdot 3SO_3$	$(NO_2^+)_2$	$(S_3O_{10}^{2-})$	L + K; G + E.
$N_2O_5 \cdot 4SO_3$	$(NO_2^+)_2$	$(S_4O_{13}^{2-})$	
$N_2O_5 \cdot 2SO_3$	$(NO_2^+)_2$	$(S_2O_7^{2-})$	G
$N_2O_3 \cdot 3SO_3$	$(NO^+)_2$	$(S_3O_{10}^{2-})$	G + E
$HNO_3 \cdot 2SO_3$	(NO_2^+)	$(HS_2O_7^{2-})$	G

G = Goddard et al 1950

G + E = Gerding & Eriks 1952

L + K = Lehmann & Kluge 1951

It will be seen that these reactions fall into the same pattern as the nitrogen oxide/strong acid reactions in that dinitrogen trioxide adducts yield only nitrosonium compounds dinitrogen pentoxide adduct give only nitronium compounds, and dinitrogen tetroxide gives mixed species.

The reaction between sulphur dioxide and dinitrogen tetroxide (Hart-Jones et al 1929) is slightly different, due to the susceptibility of sulphur dioxide to oxidation; the product is nitrosonium pyrosulphate $(NO)_2S_2O_7$, so an oxidation-reduction must have occurred.

It is significant that all the nitrosonium and nitronium sulphates prepared so far, contain polymeric anionic species. No $(NO)_2SO_4$ is known (Hart-Jones et al 1929), neither has $(NO_2)_2SO_4$ been isolated in the solid

state, though in the former case the hydrogen sulphate $NO.HSO_4$ is well known. No explanations have been put forward for this, though possibly the high tendency of SO_4 tetrahedra to catenate is contributary; the role of the cations is not clear.

Lehmann & Kluge (1951) have put forward tentative reaction mechanisms for the salts formed involving initial adducts formation, followed by heterolytic dissociation; this seems unlikely in the instances where sulphur trioxide is reacted with nitrates or nitrates. Also, taking the formation of nitrosonium pyrosulphate as an example, the reaction proceeds fairly slowly, and a mechanism involving ions might serve equally, since the concentrations of ions in liquid dinitrogen tetroxide and sulphur dioxide are known to be small.

Selenium Oxide/Nitrogen Oxides.

One of the earliest nitrosonium salts to be made was $(NO)_2SeO_4$ (Lenher & Matthews 1906) who prepared it by reaction of excess liquid dinitrogen tetroxide with 83% selenic acid; a blue solid crystallises out, decomposing above -13°C. The deep blue colour suggests that this may not be $(NO^+)_2$ (SeO_4^{2-}) but may contain covalently bonded nitrosonium groups also this coloration

could be due to the $N_2O_2^+$ ion, but this would put the selenium atom in unusual oxidation state.

The selenium analogue to nitrosyl hydrogen sulphate was prepared by Meyer & Wagner (1922) by reaction of excess dinitrogen trioxide with pure selenic acid. This is analogous to the dissociation of dinitrogen trioxide in sulphuric acid to give NO^+ and HSO_4^- ions. $NO.HSeO_4$ is much more static than $(NO)_2SeO_4$ but less so than the hydrogen sulphate.

The reactions of selenium trioxide with nitrogen oxides are similar to those with sulphur trioxide except that no mixed nitrosonium-nitronium species could be formed. (Kempe et al 1964).

$$SeO_3/N_2O_5 \longrightarrow (NO_2)_2Se_3O_{10}$$

$$SeO_3/N_2O_3 \longrightarrow (NO)_2Se_2O_7$$

The latter product, with a limited amount of water, gave $NO^+.HSe_2O_7^-$. These compounds were all assigned their structures on the basis of Raman spectra.

Attempts to prepare nitronium selenate or the hydrogen selenate were unsuccessful (Goddard et al 1950). The compound (NO_2^+) $(HSe_2O_7^-)$ was formed, possibly because the dissociation:-

$$2(NO_2^+)(HSeO_4^-) \longrightarrow (NO_2^+)(HSe_2O_7^-) + HNO_3$$

occurs.

EXPERIMENTAL

Stannic Chloride/Nitric Oxide.

Nitric oxide, formed by the reduction of sodium nitrate solution with ferrous sulphate (Inorganic Syntheses Vol 2, p.126), was bubbled into stannic chloride/carbon tetrachloride solution for approximately 30 minutes. The white solid analysed largely as stannous chloride.

Found:- Sn:33.1% Cl:65.0%; Stannous chloride requires Sn:36.8%Cl:63.2%.

Stannic Chloride/Dinitrogen tetroxide.

Excess dinitrogen tetroxide was prepared as mentioned before, and redistilled twice over phosperus pentoxide in vacuo, before being condensed into a Carius tube containing distilled stannic chloride, frozen down in vacuo. The tube was sealed off and the reaction mixture allowed to come up to room temperature. The gaseous products were pumped off after freezing down the reaction again and opening the Carius tube, and the solid residue examined. The analysis of freshly prepared samples corresponded roughly to a 1 : 1 $(NO)_2SnCl_6$. $Sn(NO_3)_4$ mixture.

Calculated: Sn 31.4% Cl28.3% total N 12.7% NO_3^- 33.0%

Found : Sn 33.1% Cl24.7% total N 15.2% NO_3 30.0%

Phosphorus Pentafluoride/Nitric Oxide.

Phosphorus pentafluoride was prepared by heating Phosflorogen (Ozark-Mahoning Co.Ltd.,) and condensing out the impurities in acetone/CO_2; it was purified by redistillation at c.-78°C. Nitric oxide was prepared as before and the two reactants condensed into a bomb in vacuo; at -196° C. The reaction was allowed to come up to room temperature, then the bomb was evacuated and the solid product examined.

Phosphorus Pentafluoride/Dinitrogen tetroxide.

The two reactants were prepared as before, redistilled separately in vacuo over phosphorus pentoxide and condensed into a Carius tube at -196°C. After raising to room temperature, at which stage reaction occurred, the system was recooled to 198° and the gas products pumped off and the solid products examined

Phosphorus trichloride or Phosphorus oxychloride/ dinitrogen tetroxide.

Phosphorus trichloride and dinitrogen tetroxide were condensed in a Carius tube as in other systems and the reaction allowed to come to room temperature. Phosphorus oxychloride was isolated amongst the volatile products by fractionation in vacuo, after removal of

excess dinitrogen tetroxide and nitrosyl chloride at -23°C (carbon tetrachloride slush bath) and characterised by its melting and boiling points (lit 1.25°C; found 0.9°C.(M.P.): lit: 105.1°C found: 105.0°C (B.P.))

The solid product from the phosphorus oxychloride/dinitrogen tetroxide reaction, obtained in the similar manner to the other reactions, and was analysed:-

Found (%) P:21.49 N: 9.86 Cl:25.50. $(PO_4NCl)_n$ requires
P:21.38 N: 9.70 Cl:25.49

Arsenic Trichloride/Nitrosyl Chloride

Nitrosyl chloride, prepared as previously, was dried over phosphorus pentoxide in vacuo and condensed, in excess, into a Carius tube containing distilled arsenic trichloride, in vacuo at -196°C. The reaction mixture was raised to room temperature. On evacuation of the reaction mixture the white solid was soon to dissociate. The red liquid was condensed in a trap at -78°C, and the system opened to the atmosphere. On raising the room temperature, excess nitrosyl chloride boiled off.

Analysis of red liquid: Found(%) As: 29.0 Cl: 56.2
N: 5.8

$AsCl_4.NO$ requires As: 29.8 Cl: 56.4
N: 5.5

Arsenic Trichloride/Dinitrogen Tetroxide.

Arsenic trichloride and dinitrogen tetroxide were separately vacuum distilled into a Carius tube, which was then sealed, and the reaction mixture raised to room temperature. A white solid rapidly precipitated out at room temperature. After evacuation of excess solvent, this was transferred to the dry box and examined.

Analysis Found:	As: 21.0	N: 19.5	NO_3: 71.1
$As(NO_3)_3.2N_2O_4$ required	As: 21.3	N: 19.9	NO_3: 71.3

Antimony Pentachloride/Nitric Oxide.

A stream of nitric oxide was bubbled through an antimony pentachloride (5 gms)/ carbon tetrachloride (100 mls) solution for 30 - 40 minutes. The yellow solid product was filtered by suction in a dry box, then vigorously removed of all traces of solvent in vacuo. It was then examined by infrared spectroscopy, and analysed.

Analysis found (%)	Sb : 39.3	Cl : 47.0	N : 4.6
$SbCl_4.NO$ requires	Sb: 39.5	Cl : 46.8	N : 4.6

At concentrations of antimony pentachloride in the region of 10 gms/100 mls carbon tetrachloride, or above, significant quantities of $NO.SbCl_6$ started to be formed.

Antimony pentachloride/Dinitrogen tetroxide.

These were reacted in a Carius tube in a similar manner to the $SnCl_4/N_2O_4$ reaction, and the gaseous products removed in vacuo, and the solid products examined.

Analyses of the reaction product mixtures were highly inconsistent, but there was considerable residual chlorine in all cases.

Dinitrogen tetroxide/Sulphur dioxide.

These reactants, separately dried in vacuo, were condensed in a Carius tube and reacted at room temperature for about 24 - 30 hours. The solid residue had a purple tinge due probably to $N_2O_2^+$ ion formation; on pumping down this vanished, leaving $(NO)_2S_2O_7$

Found	(%)	N : 11.5	S : 26.6
Calculated for $(NO)_2S_2O_7$		N : 11.7	S : 26.9

CHAPTER IV

REACTIONS OF NITROGEN OXIDES AND NITROSYL HALIDES WITH COMPOUNDS OF TITANIUM AND ZIRCONIUM

The Group IV Elements Titanium, Zirconium.

The first studies on the behaviour of titanium compounds in nitrosylating systems were by Rheinboldt & Wasserfuhr (1927), who prepared $(NO)_2TiCl_6$ by reaction of titanium tetrachloride and nitrosyl chloride in carbon tetrachloride solution. This has been shown, in Chapter I, to be $(NO^+)_2(TiCl_6^{2-})$.

Partington & Whynnes (1949) demonstrated that the same product $(NO)_2TiCl_6$ was obtained from reacting nitrosyl chloride with either titanium tetrachloride or trichloride.

In addition they carried out the reaction between dinitrogen tetroxide and titanium tetrachloride and reported that the products were probably a mixture of the adduct $(NO)_2TiCl_6$ and titanium dinitrate $Ti(NO_3)_2$. The existence of the latter compound seems highly questionable since the Titanium (II) oxidation state is a very strong reducing agent, and with a highly oxidising group like the nitrate anion present,

immediate oxidation-reduction of the type

$$Ti(NO_3)_2 \longrightarrow TiO_2 + N_2O_4$$

seems very probable.

The formation of $(NO)_2TiCl_6$ would be due to reactions of the type

$$TiCl_4 + 4N_2O_4 \longrightarrow Ti(NO_3)_4 + 4NOCl$$
$$2NOCl + TiCl_4 \longrightarrow (NO)_2TiCl_6$$

Gutmann & Tannenberger (1956) confirmed the formation of $(NO)_2TiCl_6$ in the titanium tetrachloride/dinitrogen tetroxide reaction system; they attempted to prepare titanium tetranitrate by reaction of the tetraiodide with dinitrogen tetroxide.

$$TiI_4 + 4N_2O_4 \longrightarrow Ti(NO_3)_4 + 4NO + 2I_2.$$

Nitrosyl iodide is unknown, hence no undesirable side-reactions, involving a nitrosyl halide, could occur. They believed that titanium tetranitrate was a product of this reaction but above 10°C it dissociated.

$$Ti(NO_3)_4 \longrightarrow TiO(NO_3)_2 + N_2O_4 + \tfrac{1}{2}O_2.$$

The residue, titanium oxydinitrate, was a white hygroscopic solid. No structural studies have been carried out on this compound. It is interesting to note that it apparently shows no tendency to form adducts of the type $TiO(NO_3)_2.N_2O_4$.

However, the compound $Ti(NO_3)_4$, tetranitrato-titanium, has been prepared by the reaction of hydrated titanium tetranitrates with dinitrogen pentoxide (Field & Hardy 1963 b). Infra-red examination showed the compound to be covalent, containing nitrato-groups. The splitting V_4-V_1 was 401 cm^{-1}, showing the compound to be highly covalent. It has a low melting point, 58°C, as would be expected for a highly covalent compound. Field & Hardy noted that in nujol mulls, the compound decomposed even over the period during which the spectrum was run. This has been noticed with similar compounds in the present work. Reaction with n-dodecane gave alkylnitrate and nitroalkane fractions, probably due to the tendency of nitrato-groups to radical dissociation.

$$M - O - N\begin{matrix}O\\ \diagup\\ \diagdown\\ O\end{matrix} \longrightarrow \dot{M} - O + \dot{N}O_2$$

as has been mentioned by Addison (1962).

$\underline{(NO)_2TiF_6}$

The preparation of nitrosonium fluotitanate $(NO)_2TiF_6$ has been attempted previously by the reaction of titanium metal with bromine trifluoride to yield titanium tetra-fluoride followed by further treatment

with bromine trifluoride and nitrosyl chloride (Woolf 1950). It was found that the product was a mixture of $(NO)_2TiF_6$ and $TiF_4.x\ BrF_3$. In the present work nitrosonium chlorotitanate was dissolved in bromine trifluoride, and the excess of solvent removed. The product, as with Woolf, was a mixture of $(NO)_2TiF_6$ and $TiF_4.xBrF_3$. Infra-red examination showed a band at 2308 cm^{-1}, which would almost certainly be due to nitrosonium ion in $(NO)_2TiF_6$; the bromine trifluoride impurity is probably present as $(BrF_2^+)_2(TiF_6^{2-})$. The BrF_2^+ ion has been postulated as occurring in the bromine trifluoride solvent system (Woolf 1950).

Zirconium

By direct reaction of zirconium tetrachloride and nitrosyl chloride, Devin & Perrot (1958) obtained $(NO)_2ZrCl_6$. The present work confirmed this; $(NO)_2ZrCl_6$ is a pale yellow powder, fairly hygroscopic, and an infra-red band at 2188 cm^{-1} confirmed the existence of free nitrosonium ion so that the compound could be formulated $(NO^+)_2(ZrCl_6^{2-})$.

Reaction of zirconium tetrachloride and nitrosyl chloride in bromine trifluoride gave $(NO^+)_2(ZrF_6^{2-})$; this was confirmed by the presence

of an infra-red band at 2310 cm^{-1}. It was observed that the fluo-salt was much less stable to hydrolysis than the chloro-salt. This has been noted before in the cases of the corresponding stannates and antimonates. Also, in the present case, the nitrosonium ion absorption again occurs at a much higher frequency in the fluo- than the chloro- derivative.

No reactions were carried out between zirconium tetrachloride and dinitrogen tetroxide, but the reaction with dinitrogen pentoxide is known to give tetranitrato-zirconium, $Zr(NO_3)_4$ (Field & Hardy 1962).

$$4N_2O_5 + ZrCl_4 \longrightarrow Zr(NO_3)_4 + 4NO_2Cl$$

Like its titanium analogue, the zirconium compound has been shown to contain co-ordinated nitrato-groups. In this case the V_4-V_1 splitting is approximately 350 cm^{-1}, considerably less than that observed in the titanium compound, but still indicative of strong covalent character.

In all the above examples involving the group IVA metals, the metals are invariably in the +4 oxidation state, which is much the most stable state for these metals.

EXPERIMENTAL

$(NO)_2TiCl_6$

This preparation is described in the experimental section of Chapter I.

$(NO)_2TiF_6$

Nitrosonium chlorotitanate was prepared as before, and about 1.5 gm placed in a silica reaction flask; then bromine trifluoride was added, with the mixture cooled down to about -20° (carbon tetrachloride slush-bath). The mixture was allowed to rise to room temperature and the excess bromine trifluoride was then removed in vacuo at 80°-90°C. A white,faintly brown powder remained. Hydrolysis, and addition of silver nitrate solution, showed that some bromine was present.

Analysis:

N:12.9% Ti:23.2% $(NO)_2TiF_6$ requires N:14.6% Ti:25.0%

$(NO)_2ZrCl_6$

Nitrosyl chloride, dried by distillation over phosphorus pentoxide in vacuo, was transferred into a Carius tube containing zirconium tetrachloride, by vacuum distillation. The tube was sealed and the mixture allowed to rise to room temperature, when

reaction took place. The mixture was frozen down and the excess nitrosyl chloride removed in vacuo. A yellow solid remained.

Analysis:

N:7.4% Cl:58.6% $(NO)_2ZrCl_6$ requires N:7.7% Cl:58.5%

$\underline{(NO)_2ZrF_6}$

Nitrosyl chloride, dried as before, was transferred by vacuum distillation into a silica reaction flask containing zirconium tetrachloride; this was removed from the vacuum system and cooled to - 184°C, then bromine trifluoride was added. The mixture was allowed to come up to room temperature, when reaction took place, then the excess volatile products were removed in vacuo at 80°-90°C. A white solid remained.

Analysis:

N:10.3% F:42.8% $(NO)_2ZrF_6$ requires N:10.6% F:43.2%

In this case the product showed no trace of bromine.

Infra-red spectra were measured, as previously, on a Grubb Parsons DB1 spectrophotometer, and the spectra were measured as mulls in florube grease. The quoted nitrosonium ion frequencies were calibrated against polystyrene.

CHAPTER V

THE GROUP VA METALS. VANADIUM, NIOBIUM, TANTALUM

1. Vanadium.

Vanadium is known to exist in the oxidation states -1, 0, +2, +3, +4, +5. In addition, it has a strong tendency to form vanadium-oxygen multiple bonds of high bond strength in systems containing oxygen-donor groups. The stability of the vanadium-oxygen bond has a important effect in vanadium preparative chemistry. When dealing with a system containing vanadium-oxygen bonding, it is often very difficult to obtain oxygen-free vanadium compounds. Hence, the best characterised state of vanadium (IV) is as the vanadyl, VO^{2+} cation; also, several vanadium (V) compounds containing the VO (III) group are well known, e.g. the oxytrihalides VOF_3 and $VOCl_3$, and more recently, compounds containing the VO_2^+ group have been characterised. (Pantonin et al 1960).

It has been noted, in chapter I, that the V-O bonds in vanadium pentoxide can be broken by nitryl fluoride (Aynsley et al 1954, & Hetherington and

Robinson 1957) and by the nitrosyl chloride/bromine trifluoride system (Woolf 1950). Probably in the latter case the fluorinating agent is nitrosyl fluoride, since the simple vanadium pentoxide/bromine trifluoride system gives the oxytrifluoride VOF_3. If this is the case, the fluorination reactions could be of the type:-

$$VOF_3 + 2NO_2F \longrightarrow VF_5 + N_2O_5 \quad (\text{Or } 2NO_2 + \tfrac{1}{2}O_2)$$

$$VOF_3 + 2NOF \longrightarrow VF_5 + NO + NO_2$$

The free energies of formation of the nitrogen oxide species NO and NO_2 may be the driving force of the reaction, supplying the energy for V-O bond cleavage. This suggests that pure alkali-metal hexafluorovanadates could be obtained by a reaction system of the type $NaVO_3/NOCl/BrF_3$.

Another method of 'deoxygenation' of vanadyl compounds was discovered in the course of the present work, in an attempt to prepare anhydrous vanadyl chloride $VOCl_2$. The use of thionyl chloride as a dehydrating agent to convert transition metal chloride

hydrates into the anhydrous transition metals is well known (Inorganic Syntheses, Vol. 5, p.153), and this method was attempted using vanadyl chloride hydrate and thionyl chloride. The expected reaction

$$VOCl_2.5H_2O + 5SOCl_2 \longrightarrow VOCl_2 + 5SO_2 + 5H_2O.$$

did not occur.

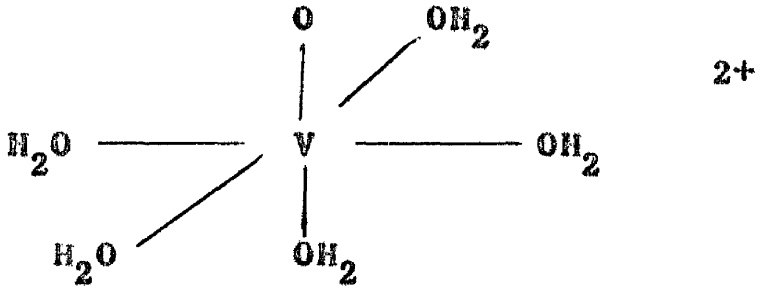
Instead, the products were vanadium trichloride, a little vanadium tetrachloride or oxytrichloride, and sulphuric acid. It was difficult to ascertain whether vanadium tetrachloride or oxytrichloride was produced. Both are volatile compounds, and in the pure state the latter is yellow and the former red. However, when vanadium oxytrichloride is slightly impure, it readily turns red and so is difficult to distinguish visually between the two.

The reaction may have proceeded either by

a) initial formation of anhydrous vanadyl dichloride, then reaction of this giving vanadium trichloride.

or b) simultaneous removal of the oxo-oxygen with one or more of the water molecules.

The structure of the aquated vanadyl ion is /



with the V=O bond length much shorter than the V-OH_2 bond lengths. The visible and ultraviolet spectra of the vanadyl ion have been satisfactorily interpreted on this basis (Ballhausen & Gray, 1961). Hence it is possible that the V-OH_2 bonds would be cleaved before the V=O bond is cleaved. The presence of sulphuric acid indicates that the sulphur has been oxidised from +4, in thionyl chloride, to +6. The corresponding reduction is

$$V(IV)O^{2+} \longrightarrow V^{3+}(III)$$

It was not possible to stop the reaction at an intermediate stage to obtain anhydrous vanadyl chloride, which suggests that reaction b , above, may be the one that occurs.

However, for a proper reaction mechanism study, the reaction between anhydrous vanadyl chloride and thionyl chloride would need to be examined; in addition, the other products of reaction would have to be identified more accurately than in the present instance.

Vanadium-nitrosonium complexes are known. The compound $K_5\ V(CN)_5NO$ gives an infra-red band at 1575 cm^{-1} which is attributed to a V NO^+ linkage. (Hieber & Jahn 1958).

Also, the nitrosonium and nitronium fluoro-vanadates have been mentioned previously (Chapter I). In the literature, the reactions between nitric oxide and vanadium tetrachloride in liquid, solution and gas phases have been reported (Whittaker & Yost 1949); no structural information was given.

The System Vanadium Trichloride/Nitrosyl Chloride.

These compounds react readily to give a mixture of purple solids, identified as $NO.VCl_4$ and $NO.V_2Cl_7$; both these compounds were reported by Whittaker & Yost (1949). They arise from the reactions:-

$$NO.Cl + VCl_3 \longrightarrow NO.VCl_4$$

$$NO.VCl_4 + VCl_3 \longrightarrow NO.V_2Cl_7$$

There was no evidence for compounds of the type $(NO)_2VCl_5$ or $(NO)_3VCl_6$. The proportions of the compounds formed obviously depended on the ratios of the original components. In dilute solutions (VCl_3:NOCl mole ratio = c.1:3) the bulk product was $NO.VCl_4$. When the ratio of the components approached

unity, the formation of $NO.V_2Cl_7$ was favoured; in all cases, however, both products were formed and an equilibrium

$$NO.VCl_4 + VCl_3 \rightleftharpoons NO.V_2Cl_7$$

may have existed.

Whittaker & Yost found that bubbling nitric oxide through liquid vanadium tetrachloride gave $NO.V_2Cl_7$; when the vanadium tetrachloride was in carbon tetrachloride solution the product was $NO.VCl_4$. This agrees with the present work, in that the former constitutes a high vanadium tetrachloride concentration giving the dimer, while the lower concentration gives the monomer form.

$NO.VCl_4$

This compound was isolated as a very deep purple crystalline solid; it was found to be exceedingly hygroscopic and hydrolysed appreciably even when being handled in the dry-box.

It sublimed completely at 30°-$35^{\circ}C$, in vacuo, and this was taken to imply the existence of covalent species probably containing $V\langle-NO^+$ bonds.

The infra-red spectrum gave a band at 2179 cm^{-1}, and a further band at 1800 cm^{-1}; time-dependence studies showed that the latter band was a decomposition band, probably due to nitrosyl chloride. The N-O bond in nitrosyl chloride absorbs at 1799 cm^{-1} (Burns & Bernstein 1950). This behaviour has been observed before in the compounds $NO.AlCl_4$, $NO.ZnCl_3$, $NO.HgCl_3$, $NO.BiCl_4$, $NO.MnCl_3$ and $NO.FeCl_4$; in all cases it was attributed to the same behaviour.

The 2179 cm^{-1} band is at the lower end of the free nitrosonium region, which indicates considerable interaction; this interaction would explain the volatility of the compound, while the predominantly ionic formulation at room temperature can account for the solubility in polar solvents such as nitrosyl chloride and sulphur dioxide, and the insolubility in non-polar solvents, e.g. carbon tetrachloride, as reported by Whittaker & Yost (1949).

The existence of the nitrosonium ion necessitates the species be formulated $(NO^+)(VCl_4^-)$. The VCl_4^- anion contains vanadium (III); in this oxidation state the outer electronic state of the vanadium ion is d^2, and it should give a characteristic d-d absorption spectrum.

The vanadium (III) ion has been obtained in tetrahedral co-ordination by substitution in a $CsAlCl_4$ host lattice, in which the aluminium is assumed to be tetrahedrally surrounded by chlorine atoms (Gruen & Gut 1961). In addition, $(C_2H_5)_4N.VCl_4$ has been reported (Scaife, 1959) and its ultraviolet and visible spectrum is stated as being markedly different from octahedrally co-ordinated vanadium (III), but no details of band positions were given.

Calculations for a d^2 field in a tetrahedral environment predict two $^3T_2$ levels at 16,000 cm^{-1} and 9,000 cm^{-1} (625 mμ and 1,110 mμ) and a $^3T_1$ level at 5,000 cm^{-1} (2,000 mμ); this is based on pure crystal field calculations assuming V^{3+} and Cl^- ions (Liehr & Ballhausen 1959).

Table 1 and the diagrams of spectra (Diagrams 1 ⟶ 4) indicate that wide discrepancies exist between theoretical data and the experimental data on the compounds cited. This is explained as being due to vanadium-chlorine covalent bonding, which will obviously affect the energy level system of the anion. (Gruen & Gut 1961). This explanation can also be used to account for the further discrepancies observed in the $NO.VCl_4$ compound.

In the spectrum of VCl_4^- in $NO.VCl_4$, the bands at 670 mμ and 960 mμ are very similar to the 667 mμ and 985 mμ bands of the $V^{3+}/CsAlCl_4$ system. In $NO.VCl_4$, the band at 870 mμ could be due to octahedral vanadium (III) species, brought about by hydrolysis.

The other bands, at 580 mμ and 420-430 mμ are probably characteristic of VCl_4^- in $NO.VCl_4$.

Irregularities in the VCl_4^- anion in $NO.VCl_4$ can be brought about in two ways:-

1) Nitrosonium ion-chlorine interaction can distort the tetrahedral symmetry of the anion, and thus the energy levels of the anion will be affected.

2) Nitrosonium Ion-Vanadium Interaction. If this occurred, a structure based partially on 5-co-ordination would be formed, and this would affect the energy levels of VCl_4^- anion very much.

Despite these, it seems highly probable that $NO.VCl_4$ contains the VCl_4^- anion, albeit non-tetrahedral due to interactions of the types 1) and 2) above.

Reaction of $NO.VCl_4$ with tetraethyl ammonium chloride gave blue crystals of $(C_2H_5)_4N.VCl_4$.

$$NO.VCl_4 + (C_2H_5)_4N.Cl \longrightarrow (C_2H_5)_4N.VCl_4 + NOCl.$$

This has been prepared by Scaife (1959). From Table 1 and the spectra diagrams, $(C_2H_5)_4N.VCl_4$ bears more

resemblance to the $V^{3+}/CsAlCl_4$ than to $NO.VCl_4$. In particular the 580 mμ and 420-430 mμ are absent, indicating that they are characteristic of $NO.VCl_4$.

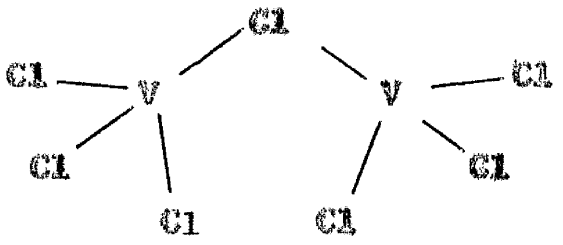
$NO.V_2Cl_7$

This compound was, like $NO.VCl_4$, isolated as a deep purple crystalline solid; it was extremely hygroscopic, and hydrolysed to give a green solution, vanadium (III).

It sublimed at a higher temperature than $NO.VCl_4$, i.e. at 66°-$70^{\circ}C$. This is in accord with the observations of Whittaker & Yost, who reported that $NO.VCl_4$ was more volatile than $NO.V_2Cl_7$.

The infra-red spectrum was indicative of a free nitrosonium ion, with a strong band occurring at 2309 cm^{-1}, notably higher than in $NO.VCl_4$. The volatility still suggests considerable anion-cation interaction.

The compound can be formulated $(NO)^{+}(V_2Cl_7)^{-}$, with the anion consisting of two VCl_4 tetrahedra bridged by one chlorine atom.



It is unlikely that the V-Cl-V bond is linear. In fact, this bond angle will probably be much nearer the value for the tetrahedral angle. If the anion be looked upon as two VCl_3 units linked by a chloride ion, this latter will probably be sp^3 hybridised, donating one pair of electrons to each of the VCl_3 units, leaving two lone pairs. On this basis, assuming absence of steric interaction between the VCl_3 groups, the V-Cl-V will be slightly less than the tetrahedral angle.

There is no spectroscopic evidence that, in the $V_2Cl_7^-$ anion, vanadium is six-co-ordinate.

Some similarities should exist between the VCl_4^- and $V_2Cl_7^-$ anions but important differences are likely due to the different symmetries. A comparison of the spectra of $NO.VCl_4$ and $NO.V_2Cl_7$ shows this.

The most important differences are -

1) The disappearance of the band C.670 mμ present both in $NO.VCl_4$ and the $V^{3+}/CSAlCl_4$ system.

2) The disappearance of the 420-430 mμ shoulder present in $NO.VCl_4$, and the appearance of a shoulder at 490 mμ.

3) The splitting of the 580 mμ band of $NO.VCl_4$ into two components in $NO.V_2Cl_7$ at 570 mμ and 620 mμ .

This may be an instance in which interaction between the two VCl_3 groups causes splitting of one of the transitions.

It is not sufficient to account for the differences in the spectra of $NO.VCl_4$ and $NO.V_2Cl_7$ in terms of the different symmetries of the two ions. As has been pointed out, the VCl_4^- anion in $NO.VCl_4$ probably undergoes considerable distortion due to anion-cation polarisation; this distortion will effect the transitions in the d-d spectrum. Anion-cation polarisation is probably very important in $NO.V_2Cl_7$ as its volatility would suggest; it is very unlikely that polarisation by the nitrosonium ion will affect the two anions equally. In particular, the greater size of the $V_2Cl_7^-$ anion will alter the charge distribution throughout the lattice. This may be one of the causes of the large difference between the nitrosonium ion stretching frequencies in the two cases. Since the ratios NO^+:Cl and NO^+:V are different in both cases, these types of interaction are most unlikely to affect both anions equally.

The reactions between vanadium trichloride and nitrosyl chloride invariably yielded a small quantity of a pale green residue. This residue was involatile,

and hydrolysed with mild effervescence. The infra-red spectrum showed a strong band at 2326 cm^{-1} and rather broad bands at about 1100 cm^{-1} and 1000 cm^{-1}. No other bands were present.

It seems reasonable to assign the 2326 cm^{-1} band to free nitrosonium ion; the bands at 1100 cm^{-1} and 1000 cm^{-1} may have been due to vanadium-oxygen double bonds. It has been shown that vanadium-oxygen bonding systems do absorb in this region (Barraclough et al 1959).

Analysis suggests that the product is mainly $NO.VOCl_4$. However, the nitrosyl chloride/vanadium oxytrichloride gives no evidence of compound formation, so that the existence of $NO.VOCl_4$ is highly doubtful.

The compound is probably formed when the vanadium trichloride/nitrosyl chloride solid reaction product mixture is transferred in the dry-box, from the Carius tube to the sublimer. Although this operation was carried out as rapidly as possible it was inevitable that some contact with slightly moist air occurred and so hydrolysis could take place.

The infra-red spectroscopic data suggests very strongly that the VCl_4^- and $V_2Cl_7^-$ anions are much more susceptible to hydrolysis than is the nitrosonium ion.

Whittaker & Yost (1949) isolated one further compound from the nitric oxide/vanadium tetrachloride reaction system. In the gas phase, the two compounds reacted to give $V_2Cl_8.(NO)_5$. No such compound was isolated in the vanadium trichloride/ nitrosyl chloride reaction.

The difference between gas and liquid phase reactions involving nitrosyl chloride nitrogen dioxide has already been noted. In the liquid phase, these behave as ionising solvents

$$NOCl \rightleftharpoons NO^+ + Cl^-$$

$$2NO_2 \rightleftharpoons N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

whereas in the gas phase, they behave as molecular or radical-molecular species. However nitric oxide behaves both in gas and liquid phase reactions as a radical-molecule. Thus with the vanadium tetrachloride/ nitric oxide system the species should be independent of the phase, but apparently the mechanism of reaction does depend on the phase; it is possible that the compound $V_2Cl_8(NO)_5$ contains $V \leftarrow NO^+$ linkages.

The extreme volatility of ionic compounds such as $NO.VCl_4$ and $NO.V_2Cl_7$ is obviously interesting, but it has been noticed previously, in the case of $(NO)_2TiCl_6$; this ionic compound sublimes readily at room temperature.

It is not essential that the species existing in gas and solid phases are identical, and it is possible that $NO.VCl_4$ sublimes as a five co-ordinate covalent species. This has been postulated to occur with the adduct $Fe(NO_3)_3.N_2O_4$, which, it has been suggested, exists in the vapour phase as $Fe(NO)(NO_3)_4$ involving penta-co-ordinate iron similar to iron pentacarbonyl (Addison et al 1958).

It is unlikely that $NO.VCl_4$ sublimes with dissociation, though this could occur with $(NO)_2TiCl_6$

$$NO.VCl_4 \longrightarrow VCl_3 + NOCl \qquad A$$

$$(NO)_2TiCl_6 \longrightarrow TiCl_4 + 2NOCl \qquad B$$

In reaction A , dissociation would lead to deposition of involatile vanadium trichloride. In B , both titanium tetrachloride and nitrosyl chloride are volatile and dissociation could occur, with recombination on coding. Hence, it seems probable that $NO.VCl_4$ and $NO.V_2Cl_7$ do exist in the vapour phase as molecular species, though in the solid state they are definitely ionic, with some covalent character.

It is possible, that in reaction A , $NO.VCl_4$ may dissociate to give VCl_3 monomer units, which might sublime, and recombine with nitrosyl chloride on condensing.

Normally, vanadium trichloride is polymeric at room temperature (Wells, 1962, p.345).

In this context, anhydrous cupric nitrate, $Cu(NO_3)_2$ sublimes at 150-200°C; the solid state infra-red spectrum indicates covalently bonded nitrato-ligands (Addison & Gatehouse 1958) and this was interpreted as suggesting the existence of $Cu(NO_3)_2$ monomer species in the solid state. However, a crystallographic examination of anhydrous cupric nitrate indicates that it can be formulated as a polymeric structure of the type:-

$Cu(NO_3)^+ : NO_3^-$ (Wallwork 1959).

The classic example of a volatile ionic compound is ammonium chloride. This exists in the solid state as $(NH_4^+)(Cl^-)$, and sublimes as NH_3 and HCl molecular species:-

$$NH_4^+ . Cl^- \longrightarrow NH_3 + HCl.$$

Thus the volatility of a compound may not be too clear an indication of its structure in the solid state, since the possibility of structure change coincident with phase change has to be taken into account. In particular, high volatility of a solid cannot necessarily be assumed to be due to covalent, probably

monomeric species existing in the solid state.

It may be that an ionic compound will be volatile, if the ions are so situated in the crystal lattice to permit appreciable orbital overlap as the magnitude of thermal vibrations increase. Obviously, only under special circumstances will this kind of orbital overlap give rise to covalent bond formation, and it will require the presence of particularly suitable anions or cations. This is well illustrated by taking ammonium chloride as an example. When the magnitude of thermal excitation is low (i.e. at room temperature) there is little opportunity for H-Cl bond formation. However, as thermal excitation increases, the constituent ammonium and chloride ions will approach more closely, until orbital overlap between hydrogen and chloride species is sufficient to permit H-Cl bond formation.

However, it would be interesting to observe the gas phase spectra of these volatile nitrosonium salts, and, especially, the solid state spectra in the region of the sublimation temperature.

Both $NO.VCl_4$ and $NO.V_2Cl_7$ dissolve quite readily in nitrosyl chloride to give rise to solutions which are very deeply coloured reddish-brown. $NO.VCl_4$

and $NO.V_2Cl_7$ will almost certainly be ionised in such solutions, and the VCl_4^- and $V_2Cl_7^-$ ions may give rise to VCl_5^{2-} or higher species, or possibly more highly polymeric anions.

Vanadium Oxytrichloride/Nitrosyl Chloride.

No reaction appeared to take place between these components. There was no solid residue, and gas phase spectra indicated only unchanged nitrosyl chloride and vanadium oxytrichloride.

Vanadium Tetrachloride/Nitrosyl Chloride.

As with the previous system, no reaction took place between nitrosyl chloride and vanadium tetrachloride. Both starting materials were recovered unchanged.

Thus, it appears that nitrosyl chloride will not attack four-co-ordinate vanadium chloro-species; this may possibly be due to steric reasons though it does seem unlikely.

However, it is quite possible that chloride exchange occurs between the species in the VCl_4/NOCl and $VOCl_3$/NOCl systems, and this could be verified by tracer studies of the type carried out by Lewis & Sowerby (1957).

Vanadium Trichloride/Dinitrogen Tetroxide.

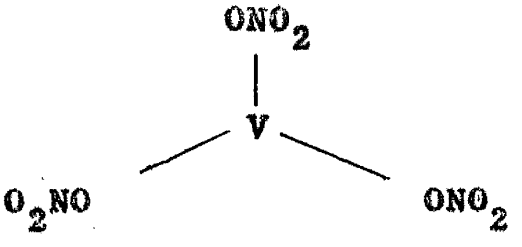
This reaction yielded a yellow-orange solid product $V\ N_3O_9$, which was originally considered to be vanadium trinitrate $V(NO_3)_3$ formed thus

$$VCl_3 + 3N_2O_4 \longrightarrow V(NO_3)_3 + 3NOCl.$$

However, chemical evidence and magnetic evidence showed that the compound was definitely vanadium (V); it reacted with water to give an orange solution which could be easily reduced with sulphur dioxide, and it was observed to have zeromagnetic moment, indicating a d^o configuration.

The following series of reactions is proposed, to explain the VCl_3/N_2O_4 reaction:-

1) Initial formation of $V(NO_3)_3$, as above; this compound could have a covalent structure of the type:-



The nitrato-ligand is a potential oxidising agent, and the oxidation of vanadium (III) to vanadium (V) would be accompanied by V-O double band formation which would facilitate the reaction:-

2) /

2) $V(NO_3)_3 \longrightarrow VO_2.NO_3 + N_2O_4$

The compound $VO_2.NO_3$ had been prepared by Pantonin et al (1960) and has been shown to contain V-O double bonding, probably in the form of the VO_2^+ ion. Then adduct formation could occur:-

$$VO_2NO_3 + N_2O_4 \longrightarrow VO_2.NO_3.N_2O_4$$

This adduct is of the same empirical composition as $V(NO_3)_3$. The compound $VO_2NO_3.N_2O_4$ is fairly hygroscopic, but quite easy to handle in the dry-box. The infra-red spectrum gave bands in the following regions:-

3360 w	1014 vs
2326 m	793 s
1601 m	713 m
1301 m	660 w
1256 s	
1149 w	(all numbers in cm^{-1})
1081 w	s - strong m - medium w - weak

The 2326 cm^{-1} band was assigned to the free nitrosonium ion; on this basis, the compound was formulated $(NO)^+(VO_2(NO_3)_2)^-$, and the bands assigned thus:-

3360	-	water band
2326	-	V_1 nitrosonium ion
1601		V_4 nitrato-group
1301, 1256		V_1 nitrato-group

1149		
1081		
1014	-	V-O stretching mode
793	-	V_6 nitrato-group
713		V_3, V_5 nitrato-group
660		

The 1301 cm^{-1} band was originally assigned to nitrogen dioxide, present as a decomposition product. The symmetrical stretching mode of nitrogen dioxide absorbs at 1298 cm^{-1}, as stated in Chapter II. However, no asymmetric mode at about 1700 cm^{-1} is present, so it is unlikely that the 1301 cm^{-1} can be assigned to the dinitrogen dioxide molecule. It is more likely that the V_1 level is split; both the 1301 cm^{-1} and 1250 cm^{-1} bands were too intense to be overtone or combinational bands, and neither were they due to decomposition products.

The 1149 cm^{-1} band could not be assigned; it was weak, and may have been an overtone or combinational band of low frequency modes. The 1081 cm^{-1} band may have been an abnormally high nitrato -V_2 mode; this mode usually absorbs between 970 cm^{-1} and 1034 cm^{-1}. However it is more likely that the very strong absorption centred about 1014 cm^{-1}, and assigned to

the V-O bond, contains the V_2 mode of the nitrato-group.

The 793 cm^{-1} band falls with the region for the V_6 vibrational mode of the nitrato-ligand, and the lower bands at 713 cm^{-1} and 660 cm^{-1} may be due to the V_3 and V_5 modes of the same ligand.

Hence, the infrared spectrum of $VO_2NO_3 \cdot N_2O_4$ can be interpreted satisfactorily in terms of a $(NO)^+(VO_2(NO_3)_2)^-$ structure, with the anion containing covalent nitrato-groups. The V_4-V_1 splitting of 300-350 cm^{-1} means that this anion is highly covalent; there is no tendency for a dissociation of the type

$$(VO_2(NO_3)_2)^- \longrightarrow VO_2NO_3 + NO_3^- \longrightarrow VO_2^+ + 2NO_3^-$$

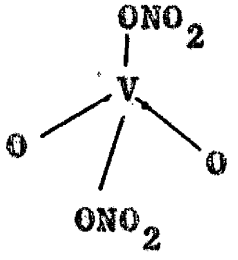
There is no infra-red evidence for nitrate ion. The absence of bands in the 1390 cm^{-1} and 830 cm^{-1} regions, corresponding to the V_3 and V_4 modes respectively, indicates that this ion is not present.

The uranyl nitrate-dinitrogen tetroxide adduct has been studied (Addison et al, 1964), and the infra-red spectrum was observed to give bands in the 2200 cm^{-1} and 2300 cm^{-1} regions. No chemical evidence was found to support a nitrosonium ion structure such as $(NO)^+$ $(UO_2(NO_3)_3)^-$, although the anion $(UO_2(NO_3)_3)^-$ is known to occur in other compounds. The 2200 cm^{-1} and 2300 cm^{-1} bands were assigned as overtones or combinational modes

on account of their weakness. However, Addison et al also observed that the dinitrogen tetroxide of the adduct $UO_2(NO_3)_2.N_2O_4$ was easily replaced by other ligands such as pyridine, and that electrolysis experiments demonstrated that the uranium was present in the cation.

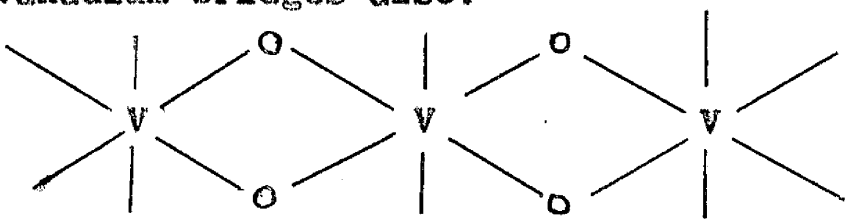
It is possible that the $VO_2NO_3.N_2O_4$ adduct has a similar structure; however, the 2326 cm^{-1} band in this adduct is too strong to be assigned to an overtone or combinational mode, and the only possible fundamental modes falling in this region are the nitrosonium V_3 mode and the nitrosonium V_1 mode. The former cannot be entirely ruled out, but the absence of a combinational band in the 3700 cm^{-1} region suggests that nitronium ion is not present.

The anion $VO_2(NO_3)_2^-$ may have a tetrahedral structure, and be essentially monomeric

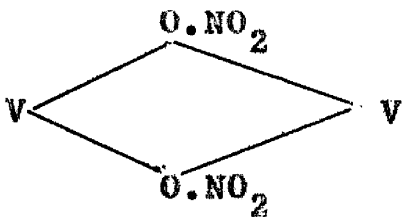


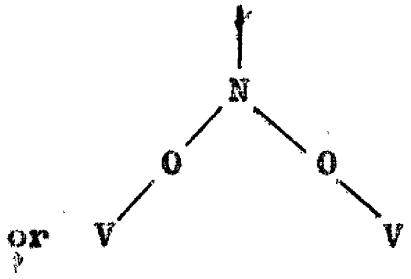
or the vanadium could be octahedrally surrounded by oxygen-atoms, giving rise to a polymeric structure which could involve simple V-O-V bridges and vanadium-

nitrato-vanadium bridges also:-



If the structure were of this nature, the vanadium-oxygen band frequencies suggest that they are double bands, non-bridging, and so would occupy the axial positions of such a structure, in which case the equatorial positions would be occupied by nitrato-groups, viz:-





As has been mentioned, the compound VO_2NO_3 is known (Pantonin et al 1960); it was thought that this compound might be obtained from $VO_2NO_3.N_2O_4$ by heating:-

$$VO_2NO_3.N_2O_4 \longrightarrow VO_2.NO_3 + N_2O_4$$

The adduct $VO_2NO_3.N_2O_4$ was heated in vacuo up to 200°C for 4-5 hours- the only solid product was vanadium pentoxide, though a mixture of nitrogen oxides, largely nitrogen dioxide, were evolved.

It has been reported that the reaction

$$UO_2(NO_3)_2 \cdot N_2O_4 \longrightarrow UO_2(NO_3)_2 + N_2O_4$$

requires highly specific conditions (Addison et al 1964), and the same probably applies to the $VO_2NO_3 \cdot N_2O_4$ dissociation.

Vanadium Oxychloride/Dinitrogen Tetroxide.

This reaction was carried out in an attempt to prepare vanadyl oxytrinitrate, by the following type of reaction:-

$$VOCl_3 + 3N_2O_4 \longrightarrow VO(NO_3)_3 + 3NOCl.$$

$VO(NO_3)_3$ has been prepared by the reaction of dinitrogen pentoxide with vanadium oxychloride or vanadium pentoxide

$$VOCl_3 + 3N_2O_5 \longrightarrow VO(NO_3)_3 + 3NO_2Cl$$

$$V_2O_5 + 3N_2O_5 \longrightarrow 2VO(NO_3)_3$$ (Schmeisser & Lutzow 1954)

and is a pale golden liquid, boiling under reduced pressure at 28^o-30^o.

Evidence of reaction in the $VOCl_3/N_2O_4$ system came from examination of the gas phase spectra during the course of the reaction; the spectra indicated the presence of nitrosyl chloride.

After the reaction was complete, and the nitrosyl chloride and dinitrogen tetroxide removed as much as possible, a yellow-brown liquid remained, which was believed to be $VO(NO_3)_3$.

However, a gas phase spectrum showed only weak bands in the 1000-1050 cm^{-1} region, where vanadium-oxygen bands normally absorb. Strong bands in the 1700 cm^{-1} and 1300 cm^{-1} regions indicated nitrogen dioxide, and a very strong band was present at 1370 cm^{-1}. These were thought to be due to the following series of reactions:-

$$VOCl_3 + 3N_2O_4 \longrightarrow VO(NO_3)_3 + 3NOCl$$

$$VO(NO_3)_3 + N_2O_4 \longrightarrow VO(NO_3)_3.N_2O_4$$

In the gas phase, the postulated adduct $VO(NO_3)_3.N_2O_4$ may dissociate to yield the reactants. Thus, bands due to nitrogen dioxide will be present in the gas phase.

Finally, reaction between the sodium chloride cell windows and the $VO(NO_3)_3$ may occur:-

$$VO(NO_3)_3 + 3NaCl \longrightarrow VOCl_3 + 3NaNO_3.$$

The strong band at 1370 cm^{-1} may be due to nitrate ion formed in sodium nitrate by the above reaction; however, if this were the case, gaseous V0(III) species would still be present as vanadium oxytrichloride, and hence infra-red absorptions in the 1000-1050 cm^{-1} mark would be expected.

The liquid was evaporated to dryness and a red solid remained, which was found to be $VO_2.NO_3$, as prepared by Pantonin et al (1960).

This was postulated to be formed thus:-

$$VO(NO_3)_3 \longrightarrow VO_2.NO_3 + N_2O_5$$

or, alternatively, the yellow-brown liquid could have been a solution of VO_2NO_3 in dinitrogen pentoxide, and evaporation to dryness merely removed the solvent. In either instance, this suggests that VO_2NO_3 does not form a dinitrogen pentoxide adduct, i.e. the nitronium ion analogue to $(NO)^+(VO_2(NO_3)_2)^-$ does not exist.

Vanadium Dibromide/Nitrosyl Bromide.

These compounds react to give an ochre-yellow solid VBr_3NO, which is hygroscopic and hydrolyses to give a vanadium (III) solution. It gives a very simple infra-red spectrum with bands at 1923 cm^{-1} and 1768 cm^{-1}; bands occurring lower in the infra-red region are compatible with reaction between Nujol, the mulling agent, and the nitrosyl group on the compound.

These bands at 1923 cm^{-1} and 1768 cm^{-1} are in the region characteristic of metal nitrosonium ion bonding; the presence of two bands in the region implies that the vanadium ⟨— nitrosonium ion system is in two different environments in the molecule. This immediately suggests a polymeric structure, since monomeric VBr_3NO would have nitrosonium ion present in one environment only. Both the frequencies are well

above those recorded for bridging nitrosonium ions (Piper & Wilkinson 1956; King & Bisnette 1964) so the nitrosonium ions present must all be terminal.

Early attempts to carry out this reaction gave a yellow-brown product, or mixture of products; the main constituent of this was finally identified as the adduct $VO_2NO_3 \cdot N_2O_4$.

This product resulted from preparations involving nitrosyl bromide prepared by the $NO.HSO_4$/NaBr reaction; as explained in Chapter II, this method yielded appreciable quantities of nitrogen dioxide, giving dinitrogen tetroxide in a liquid phase reaction. Thus the nitrosyl bromide was appreciably contaminated with dinitrogen dioxide, and this was confirmed by a gas phase spectrum of the nitrosyl bromide used.

In this context, the systems uranium/NOCl and uranium/N_2O_4 have been reported in the literature (Addison & Hodge 1961 a), together with uranium/NOCl/N_2O_4 systems. It was found that this latter system yielded only $UO_2(NO_3)_2$, unless the nitrosyl chloride percentage composition was 85% or over; in addition, $UO_2(NO_3)_2 \cdot N_2O_4$ was still one of the products of reaction until the nitrosyl chloride concentration rose above 98%. Hence, if slightly impure nitrosyl chloride gives

rise to nitrates or dinitrogen tetroxide adducts, it is reasonable to assume that $NOBr/N_2O_4$ mixtures will behave in the same way. This seems the most valid explanation of the formation of $VO_2NO_3.N_2O_4$; the reaction $VBr_2/NOBr$ occurs less readily than the reaction VBr_2/N_2O_4, again, probably due to vanadium-oxygen double bond formation supplying the free energy for reaction.

Vanadium Pentoxide/Nitrosyl Chloride.

Under specific conditions, the nature of which were not elucidated, vanadium pentoxide will react with nitrosyl chloride, over a period of 3-5 hours to give a very deep blue solid. This reaction proceeded as stated, on the first attempt, but later attempts, even on heating, gave no reaction at all, although the nitrosyl chloride solution became very faintly green due, presumably, to slight solution of vanadium pentoxide. It is possible that the reaction was brought about catalytically by small quantities of adsorbed species on the inside of the Carius tube.

The blue product was not obtained in sufficient yield for analysis; however, infra-red analysis gave a very simple spectrum:-

2300-2350	cm^{-1}	m.
1800	cm^{-1}	w.
900-920	cm^{-1}	s.

Time dependence spectra showed the 1800 cm^{-1} band to be a decomposition band, presumably due to nitrosyl chloride. The 900-920 cm^{-1} band, a broad absorption, is assigned to vanadium-oxygen banding, though it is markedly lower than the analogous mode in $VO_2NO_3.N_2O_4$; this may be because the vanadium is in a lower oxidation state in the V_2O_5/NOCl reaction product.

There is no doubt that reduction has occurred; the intense colour could be that associated with the vanadyl ion in compounds such as vanadyl sulphate. Alternatively it could be due to charge transfer occurring between different oxidation states of vanadium in the same ion.

Niobium.

Niobium is known in a less wide range of oxidation states than is vanadium. The +3 and +5 are the best characterised with niobium (III) being reducing. Vanadium (III) shows no such tendency. Thus, all the compounds dealt with in this section are compounds of niobium (V).

The compound $NO.NbF_6$ is known; it was prepared by reaction of niobium pentoxide and nitrosyl chloride in bromine trifluoride (Clark & Emeleus 1958).

In the present work, this reaction was repeated but using niobium pentachloride instead of the pentoxide. The compound was the same; it was very hygroscopic, and the presence of an infra-red absorption band at 2390 cm^{-1} confirms the structure as $(NO)^{+}(NbF_6)^{-}$.

There are no examples of the anion $NbCl_6^{-}$ reported in the literature; hence the reaction between nitrosyl chloride and niobium pentachloride was carried out. A pale yellow solid was isolated which gave an infra-red absorption at 2174 cm^{-1}; the intensity of this band diminished very rapidly with time and it was observed that the reaction product did dissociate very rapidly. Thus the reaction

$$NOCl + NbCl_5 \longrightarrow NO^{+}.NbCl_6^{-}$$

was proposed, with the high nitrosonium ion - chlorine interaction giving rise to the ease of dissociation, and the low frequency free nitrosonium ion stretching frequency.

The high instability of $NO.NbCl_6$ suggests that the niobium (V) ion is not large enough to accommodate six chlorine atoms distributed hexagonally around it. Niobium pentachloride consists of monomeric $NbCl_5$ units,

* This was later found to be incorrect: see Adams, Chatt, Davidson + Garratt, J. Chem. Soc., 1963, 2189.
The author thanks Dr. K.W. Bagnall for pointing out this error.

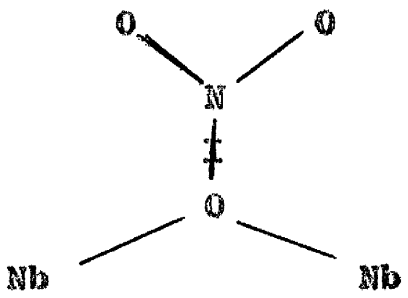
with the five chlorine atoms arranged in a trigonal bipyramid about the niobium atom (Skinner & Sutton 1940).

The reactions involving niobium pentachloride with dinitrogen tetroxide (Bagnall et al 1964) and dinitrogen pentoxide (Field & Hardy 1963 a) are reported in the literature.

The latter reaction proceeds readily to yield the compound, niobium oxytrinitrate $NbO(NO_3)_3$.

$$NbCl_5 + 4N_2O_5 \longrightarrow NbO(NO_3)_3 + 5NO_2Cl$$

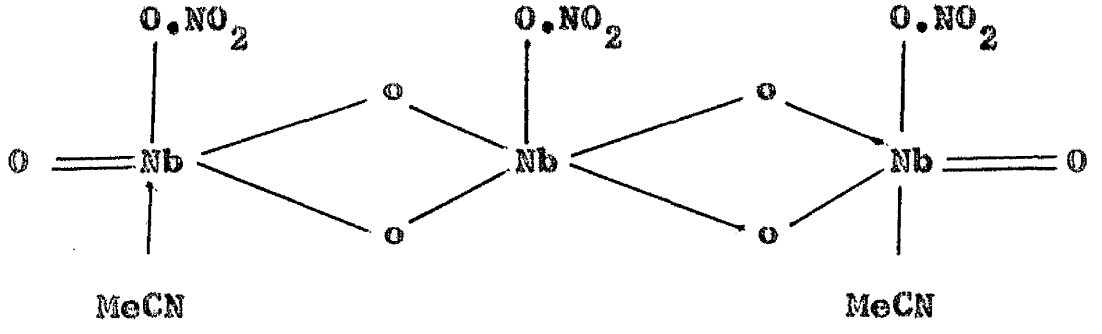
No tendency for $NbO(NO_3)_3.N_2O_5$ or $NbCl_5.NO_2Cl$ adduct formation was observed. Infra-red examination of the compound showed that covalent nitrato-ligands are present, and that niobium-oxygen double bonds exist also. The compound $NbO(NO_3)_3$ starts to decompose when heated in vacuo up to 120°C; Field & Hardy postulated it as containing niobium-oxygen double bonds and Nb-o-Nb bridging groups; those bridging groups may be present as bridging nitrato-groups, viz:-



Niobium pentachloride will only react with dinitrogen tetroxide in the present of ionising solvents, to give solvated NbO_2NO_3 species (Bagnall et al 1964). Assuming that the reactions in both cases involve attack by nitrate ion, it appears that the concentration of nitrate ion provided by dinitrogen tetroxide auto-ionisation:-

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

is unsufficient to cause formation of niobium nitrate or nitrato-species. In the presence of ionising solvents such as acetonitrile a species of the empirical formula $NbO_2NO_3.0.67MeCN$ is formed, which in moist air picks up water to give $NbO_2NO_3.0.67MeCN.0.30H_2O$. For $NbO_2.NO_3.0.67MeCN$, the formula:-



is suggested (Bagnall et al 1964). In the presence of moist air, a water molecule bonds to the central niobium atom, so that

Tantalum.

In the present context, the chemistry of tantalum is very similar to niobium. It forms a nitrosonium fluoro-salt $NO.TaF_6$ which was first prepared by Clark & Emeleus (1958); in the present work, the infra-red spectrum of nitrosonium fluorotantalate was shown to give a strong band at 2391 cm^{-1}, confirming the structure as $(NO)^+(TaF_6)^-$.

The reaction between nitrosyl chloride and tantalum pentachloride gives $NO.TaCl_6$.

$$NOCl + TaCl_5 \longrightarrow NO.TaCl_6.$$

Infra-red examination of the complex gave an absorption band at 2165 cm^{-1}, which is at the lower end of the scale for nitrosonium ion frequencies. Unlike the niobium analogue, it is fairly stable to dissociation; although the slightly lower nitrosonium ion frequency implies a greater degree of anion-cation interaction than with $NO.NbCl_6$. The enhanced stability of $NO.TaCl_6$ cannot be explained in terms of ionic radii of the niobium (V) and tantalum (V) species, since the latter would be expected to be rather smaller and so would be less able to accommodate chlorine atoms octahedrally about it. However, tantalum has extra

orbitals available which may be able to accommodate the chlorine atoms.

Metathetical reaction of tetraethyl ammonium chloride and $NO.TaCl_6$ in liquid sulphur dioxide gave beautiful white needle-like crystals of $(C_2H_5)_4N.TaCl_6$.

$$(C_2H_5)_4N.TaCl_6 + NOCl \longrightarrow (C_2H_5)_4N.TaCl_6 + NOCl.$$

The infra-red spectrum confirmed the presence of $(C_2H_5)_4N^+$ ion, and hence verified the presence of the previously unknown $TaCl_6^-$ anion.

Bagnall et al (1964) carried out the reactions of tantalum pentachloride with dinitrogen tetroxide and dinitrogen pentoxide; both reactions were analogous to the niobium reactions

$$TaCl_5 + 4N_2O_5 \longrightarrow TaO(NO_3)_3 + 5NO_2Cl.$$

Tantalum oxytrinitrate, like its niobium analogue, contains covalent nitrato-groups which may be present as bridging groups. It has less thermal stability than niobium oxytrinitrate which is postulated as being due to weaker bridging nitrato-groups.

Reaction of tantalum pentachloride with dinitrogen tetroxide proceeds only in the presence of ionising solvents, and the species produced are solvated TaO_2NO_3

species; these presumably have analogous structures to those proposed for the niobium analogues.

It is notable that in the niobium and tantalum pentachloride reactions with dinitrogen tetroxide do not yield nitrosonium ion species; this may be because in acetonitrile solution, the nitrosonium ion is solvated and is less easy to fit in a crystal lattice.

EXPERIMENTAL

1. Vanadium Trichloride.

Vanadyl dichloride hydrate was prepared by gently boiling vanadium pentoxide in concentrated hydrochloric acid for 40-50 minutes (Sidgwick (1950, p.820)) then evaporating to small bulk. After cooling, methanol was added to the deep blue solution and evaporation to small bulk repeated. On repeating this procedure 2-3 times, vanadyl chloride hydrate eventually separated out on cooling as a very dark blue mass with little evidence of crystallinity.

Calculated for $VOCl_2.5H_2O$ Cl:30.2% Found Cl:28.7%.

The rather low chlorine value indicates that methanol may be co-ordinated on to the vanadyl ion also.

About 5-6 gms. of the hydrate, or mixed methanolate-hydrate, were refluxed with 50 mls. thionyl chloride for 1½-2 hours; the bulk of the thionyl chloride was distilled off, and a further 25-30 mls. fresh thionyl chloride added, and the mixture refluxed for another 40-60 minutes. A purple residue remained, and the thionyl chloride was coloured orange-brown, which may well have been due to dissolved vanadium oxytrichloride. The bulk of the thionyl chloride distilled off readily at

75^{o}-80^{o}, but a gummy residue remained. Heating up to $150^{o}C$ would not remove this effectively so it was decided that the residual liquid would probably be sulphuric acid since it gave a positive test with barium chloride solution; this could be formed either by hydrolysis of sulphur trioxide or sulphuryl chloride

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$SO_2Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl.$$

Red-brown vapours at these most elevated temperatures indicated the presence of vanadium oxytrichloride. The solid was then filtered as dry as possible by suction, washed twice with thionyl chloride, dried by suction, and then finally washed 3 times with dry carbon disulphide, and dried by suction again. Removal of all traces of residual acid was ensured by storing the purple product in vacuo over sodium hydroxide for 18-24 hours. (Yield = 3.5-4 gms. vanadium trichloride - about 90% based on a $VOCl_2.5H_2O \longrightarrow VCl_3$ conversion).

Analysis:

Found V:32.8% Cl:67.3% VCl_3 requires V:32.8% Cl:67.2%

Vanadium Trichloride/Nitrosyl Chloride.

1-1.5 gms. vanadium trichloride, prepared as above, was transferred to a Carius tube in a dry box to avoid hydrolysis. This was evacuated and about a threefold excess of nitrosyl chloride condensed on to the vanadium trichloride by vacuum distillation. The tube was sealed and the reaction mixture allowed to rise to room temperature. A very deep red-brown solution resulted, after vigorous reaction between the two components. On evaporation of the residual liquid by vacuum distillation a purple solid remained which was observed to sublime very early into the cold trap. To avoid too great a loss of the product, the residual nitrosyl chloride was removed at c.-20°C, cooling the Carius tube in a carbon-chloride slush bath. Still under vacuum, the Carius tube was transferred to a dry-box, and the solid transferred as rapidly as possible to sublimer and re-evacuated once more. The purple solid sublimed readily onto a probe cooled to -78°C with solid carbon dioxide; sublimation of one fraction appeared to be complete at 30°-35°C and a small purple residue still remained. After removal of the most volatile fraction, the residue was heated and found to sublime at 66°-70°. A very small green residue still

remained but this could not be sublimed further.

The purple fraction subliming at 30°-35° analysed as $NO.VCl_4$.

Found N:6.0% Cl:62.4% $NO.VCl_4$ requires N:6.2% Cl:62.6%.

The purple fraction subliming at 66°-70° analysed as $NO.V_2Cl_7$.

Found N:3.2% Cl:63.5% $NO.V_2Cl_7$ requires N:3.6% Cl:63.8%.

The infra-red spectrum of $NO.VCl_4$ was found to give a strong absorption at 2179 cm^{-1}; that of $NO.V_2Cl_7$ gave a strong absorption of 2309 cm^{-1}.

In the above reaction the main product was $NO.VCl_4$ with only a little $NO.V_2Cl_7$.

When, instead of using a threefold excess of nitrosyl chloride for the reaction, the mole ratio was made approximately unity, the reaction behaved slightly differently. After removal of excess solvent and transfer of the reaction mixture to a submlimer, sublimation up to $35^{\circ}C$ gave only a very tiny yield of the product $NO.VCl_4$. The bulk of the reaction mixture sublimed at 66°-70°, again leaving a small quantity of a green residue. In this instance the analyses were -

Fraction 1) 30°-35°

Found N:6.0% Cl:62.8% $NO.VCl_4$ requires N:6.2% Cl:62.6%.

Fraction 2) 66°-70°

Found N:3.5% Cl:63.6% $NO.V_2Cl_7$ requires N:3.6% Cl.63.8%.

Fraction 1) gave a strong infra-red absorption at 2178 cm^{-1}; fraction 2) gave a strong infra-red absorption at 2312 cm^{-1}. Thus the two products are the same in both instances.

The green residue was observed to dissolve in water with mild effervescence; analyses were

1) N:5.1% Cl:58.2%.

2) N:5.7% Cl:55.9%.

$NO.VOCl_4$ requires N:5.9% Cl:59.4%.

The infra-red spectrum of the green residue gave a sharp band at 2325 cm^{-1}, and further broad bands in the 1100 cm^{-1} and 1000 cm^{-1} regions.

Tetraethyl ammonium chlorovanadate.

0.46 gms (0.002 moles) $NO.VCl_4$ and 0.33 gms. (0.002 moles) $(C_2H_5)_4N.Cl$ were put in a Carius tube. This operation was carried out in the dry-box as rapidly as possible to avoid hydrolysis of $NO.VCl_4$. It was transferred to the vacuum system and evacuated. Sulphur dioxide, from a cylinder, was dried by vacuum distillation over phosphorus pentoxide, and then transferred similarly into the Carius tube. The tube was sealed, and the

reaction mixture raised to room temperature. The reaction was shaken for 24 hours after which time the sulphur dioxide had turned brown due to the formation of nitrosyl chloride.

$$(C_2H_5)_4N.Cl + NO.VCl_4 \longrightarrow (C_2H_5)_4N.VCl_4 + NOCl$$

The sulphur dioxide and nitrosyl chloride were removed in vacuo, leaving blue $(C_2H_5)_4N.VCl_4$. This was washed with liquid sulphur dioxide in a Carius tube to remove any traces of the reactants that may have been left.

Analysis: C:28.1% H:5.5% Cl:42.1% N:3.8%

$(C_2H_5)_4N.VCl_4$ requires C:28.9% H:6.0% Cl:42.8% N:4.2%.

Vanadium tetrachloride/Nitrosyl chloride.

Vanadium tetrachloride was prepared by heating vanadium trichloride in vacuo

$$2VCl_3 \longrightarrow VCl_4 + VCl_2$$

The volatile vanadium tetrachloride fraction was condensed in a cold trap (-184°C) as a red solid. By vacuum distillation, twice, over phosphorous pentoxide it was thoroughly dried and then transferred similarly into a Carius tube. Nitrosyl chloride was vacuum-distilled separately into the same Carius tube and the tube sealed. After raising to room temperature, the

reaction mixture was frozen down and the tube opened and evacuated. No solid product was formed.

The gas mixture was analysed by infra-red spectroscopy and the spectrum was identical to that of nitrosyl chloride. A cold trap at c.-20°C condensed out a red liquid which was vanadium tetrachloride; a further cold trap at -78°C condensed out nitrosyl chloride.

There was no evidence for any reaction.

Vanadium Oxytrichloride.

This can be prepared by heating a mixture of vanadium pentoxide and aluminium trichloride at 400°C. (Inorganic Syntheses Vol. 6, p. 119).

$$V_2O_5 + 2AlCl_3 \longrightarrow 2VOCl_3 + Al_2O_3$$

The volatile vanadium oxytrichloride distils off.

The present method is a very slight modification of this in that the reaction was carried out in vacuo and thus proceeded readily at a much lower temperature (160° - 180°C). Anhydrous aluminium trichloride was sublimed in vacuo to rid it of moisture traces. It was then intimately ground up with an excess of vanadium pentoxide, previously heated to 300°-400° for 2-3 hours. The mixture was then

evacuated, and the temperature raised slowly to 160°. If the temperature increase was made too rapid it was found that instead of reaction occurring to give vanadium oxytrichloride, aluminium trichloride sublimed out of the reaction mixture. Early trials showed that aluminium trichloride always tended to sublime out, to some extent, and collect in the cold trap used for condensing vanadium oxytrichloride out. To eliminate this undesirable effect, the tube between the reaction flask and the cold trap was partially packed with dried glass wool; this measure was successful. After vanadium oxytrichloride stopped distilling over, it was redistilled twice over phosphorus pentoxide in vacuo to dry it and used for reactions. Vanadium oxytrichloride so obtained is a yellow liquid, freezing to a yellow solid, and very hygroscopic. If any traces of moisture are present during the preparation the product has a distinct reddish colouration.

Analysis:

Found V:29.3% Cl:61.2% $VOCl_3$ requires V:29.4% Cl:61.4%.

Vanadium Oxytrichloride/Nitrosyl Chloride.

Vanadium oxytrichloride, prepared and dried as above, was transferred by vacuum-distillation into a

Carius tube, and nitrosyl chloride transferred similarly into the same Carius tube. The tube was sealed and raised to room temperature. After cooling and re-opening, the tube was evacuated. No solid residue remained. A gas phase infra-red spectrum of the volatile material showed bands in the 1798-1810 cm^{-1} region, a band in the 1030 cm^{-1} region and a triplet centred about 760 cm^{-1}. A cold trap at -20°C condensed out vanadium oxytrichloride, and one at -78°C condensed out nitrosyl chloride. There was no evidence for any reaction.

Vanadium Trichloride/Dinitrogen Tetroxide.

Vanadium trichloride was prepared as described earlier in this section. Dinitrogen tetroxide was prepared as in Chapter II. 2-3 gms. of vanadium trichloride were placed in a reaction vessel (50 mls. approximately), which was evacuated. An excess of dinitrogen tetroxide was condensed on to the trichloride in vacuo at -184°C, and the reaction allowed slowly to warm. As soon as the dinitrogen tetroxide melted, reaction was observed between the components. The reaction was allowed to proceed slowly and samples of gas were taken off for infra-red analysis during the reaction. The residual solid product was a pale yellow

brown powder VN_3O_9.

Analysis:

Found V:24.5% N:20.9% VN_3O_9 requires V:24.6% N:20.3%.

This product was heated in vacuo to 200°C. A mixture of nitrogen oxides condensed in a cold trap and the residue was vanadium pentoxide.

Analysis:

Found V:54.8% V_2O_5 requires V:55.5%.

Vanadium Oxytrichloride/Dinitrogen Tetroxide.

Vanadium oxytrichloride and dinitrogen tetroxide were condensed separately into a small reaction flask, by vacuum distillation. The reaction mixture was allowed to warm up slowly and reaction appeared to take place when the components melted. Samples of the gas products were taken off from time to time. Excess of the highly volatile residue were removed in vacuo, keeping the reaction mixture at -20°C to avoid loss of volatile fractions in the reaction mixture. A yellow-brown liquid remained. Gas phase infra-red spectra showed no evidence of V=O linkages so it was evacuated to dryness and a red-brown solid obtained, analysing as VO_2NO_3.

Found: NO_3^-:35.0% V:42.3% VO_2NO_3 requires V:35.2%

NO_3^-:42.8%.

Vanadium Bromide VBr_2.

A stream of bromine, diluted with nitrogen, was bubbled through concentrated sulphuric acid to dry it. It was then passed slowly over metallic vanadium heated to 300°-400°. Reaction occurred immediately and a mixture of vanadium bromides VBr_3 and VBr_2 sublimed out of the reaction mixture. Heating was continued for a reasonable length along the reaction tube to ensure complete decomposition of vanadium tribromide to the black dibromide. The latter condensed out on the cooler parts of the reaction tube. On completion of reaction the tube was swept out with dry nitrogen and transferred to the dry-box.

For preparation of the red vanadium tribromide the bromine was heated to about 200° before passing over the vanadium. The product sublimed out as red scaly plates.

Analyses

Black V:28.2 Br:71.9 VBr_2 requires V:28.6% Br:71.4%.

Red V:18.0% Br:82.1% VBr_3 requires V:17.3% Br:82.7%

Vanadium Dibromide VBr_2/Nitrosyl Bromide.

Vanadium dibromide was prepared as above, and nitrosyl bromide as in Chapter II. The latter was dried by

vacuum distillation over phosphorus pentoxide and transferred similarly into a Carius tube containing vanadium dibromide. The tube was sealed and the reaction raised to room temperature. On removal of excess nitrosyl bromide by evacuation, an ochre-yellow solid remained. It analysed fairly well as VBr_3NO.

Found V:20.0% N:3.9% Br: 75.0%

VBr_3NO requires V:20.8% N:4.4% Br:74.7%.

It was quite susceptible to moisture, and its infra-red spectrum changed significantly with time.

Vanadium Pentoxide/Nitrosyl Chloride.

Vanadium pentoxide was rigorously dried at 300-400^{o}C and put in a Carius tube. This was evacuated, and a two-three fold excess of nitrosyl chloride was transferred into the tube by vacuum distillation. The tube was sealed and allowed to come up to room temperature. On several occasions when this reaction was attempted, no reaction occurred and the starting materials were recovered intact. On one occasion, however, removal of excess nitrosyl chloride left a small quantity of very deep blue compound. Unfortunately insufficient was available for analysis. Its infra-red spectrum was

observed. It hydrolysed vigorously with evolution of nitrogen dioxide.

The specific conditions which were responsible for the formation of the deep blue solid were not elucidated.

Vanadium Pentoxide/Dinitrogen Tetroxide.

Rigorously dried vanadium pentoxide was put in a Carius tube, evacuated, and dinitrogen tetroxide vacuum distilled into the same tube. The tube was sealed and the reaction mixture raised to room temperature. The dinitrogen tetroxide solution was very pale green, but little vanadium pentoxide had dissolved. When the tube was evacuated, the gaseous products were examined by infra-red spectroscopy.

The vanadium pentoxide was recovered unchanged.

Niobium Pentachloride/Nitrosyl Chloride.

Nitrosyl chloride was transferred by vacuum distillation into a Carius tube containing niobium pentachloride (Stauffer Chemical Coy.), and the tube sealed. The reaction mixture was raised to room temperature. On careful evacuation of the volatile products a pale yellow solid remained. Its infra-red

spectrum was measured.

Analysis:

N:3.7% Cl:64.4% $NO.NbCl_6$ requires N:4.2% Cl:63.4%.

The wide discrepancy will be due to the ease with which the compound $NO.NbCl_4$ dissociates.

Tantalum Pentachloride/Nitrosyl Chloride.

Nitrosyl chloride was transferred by vacuum distillation into a Carius tube containing tantalum pentachloride (Stauffer Chemical Coy.). The tube was sealed and the reaction allowed to rise to room temperature. After cooling, the excess nitrosyl chloride was removed in vacuo. A white solid remained, fairly stable to hydrolysis.

Analysis:

N:3.1% Cl:49.7% $NOTaCl_6$ requires N:3.3% Cl:50.1%

Nitrosonium Fluoniobiate.

This was prepared by Woolf's method (1950). Nitrosyl chloride was transferred by vacuum distillation into a Silica reaction flask containing niobium pentachloride. The flask was removed from the vacuum system after the admission of dry air, and then bromine trifluoride was added dropwise to the mixture cooled to $-184^{o}C$. After an excess of bromine trifluoride had

been added, the reaction mixture was allowed to warm slowly to room temperature. Reaction occurred vigorously, and after completion of reaction, the volatile products were removed in vacuo at 80°-90°. A white solid remained.

Analysis:

N:5.5% F:47.2% $NO.NbF_6$ requires N:5.9% F:48.1%.

Nitrosonium Fluotantalate.

Nitrosyl chloride was transferred by vacuum distillation into a silica reaction flask containing tantalum pentachloride. Dry air was admitted into the vacuum system and the flask removed. The reaction mixture was cooled to -184°C and bromine trifluoride added dropwise from a stainless steel capsule. After an excess had been added, the mixture was allowed to warm slowly to room temperature. After the reaction had ceased, the volatile products were removed in vacuo at 80°-90°. A white solid remained.

Analysis:

N:4.1% F:34.2% $NO.TaF_6$ requires N:4.3% F:35.1%.

Tetraethylammonium chlorotantalate.

0.88 gm. (0.002 moles) $NO.TaCl_6$ and 0.33 gm. (0.002 moles)$(C_2H_5)_4N.Cl$ were placed in a Carius tube; this was then evacuated and sulphur dioxide, dried by

distillation over phosphorus pentoxide, was vacuum distilled into the tube, which was then sealed. After coming up to room temperature the reaction mixture was shaken for 24 hours after which time beautiful long white needles crystallised out.

$$(C_2H_5)_4N.Cl + NO.TaCl_6 \longrightarrow (C_2H_5)_4N.TaCl_6 + NOCl$$

The excess sulphur dioxide and nitrosyl chloride were removed in vacuo; the crystals of $(C_2H_5)_4N.TaCl_6$ were washed with liquid sulphur dioxide in a Carius tube before analysis.

Analysis Found C:17.0% H:3.4% Cl:41.2%.

$(C_2H_5)_4N.TaCl_6$ requires C:17.3% H:3.8% Cl:40.6%.

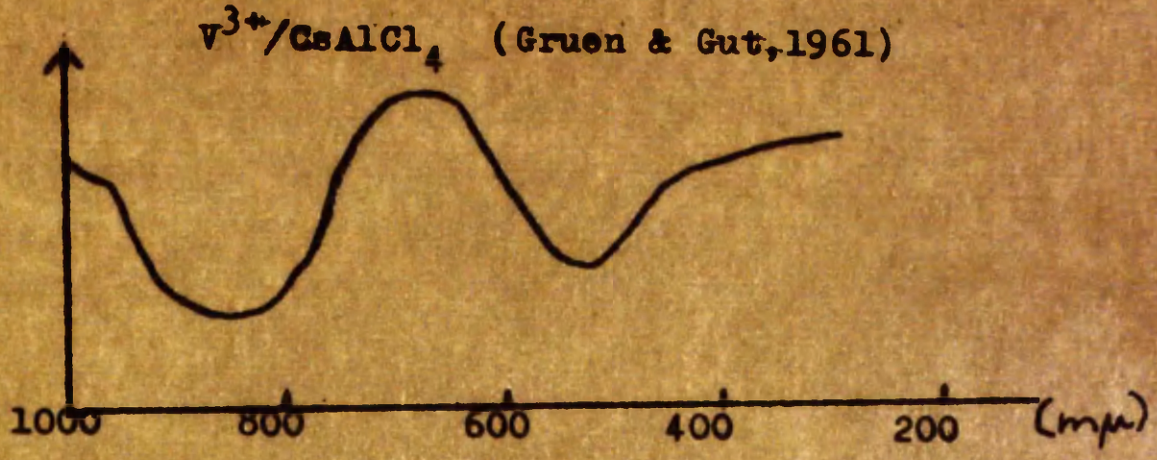
Reflectance spectra were taken of $NO.VCl_4$ and $NO.V_2Cl_7$. The compounds were diluted with rigorously dried potassium chloride and the mixtures finely ground and the reflectance cell holder packed with the mixture. This operation had to be completed rapidly to avoid excessive hydrolysis. Hydrolysis could be observed by the appearance of a distinct green colouration in the mixture.

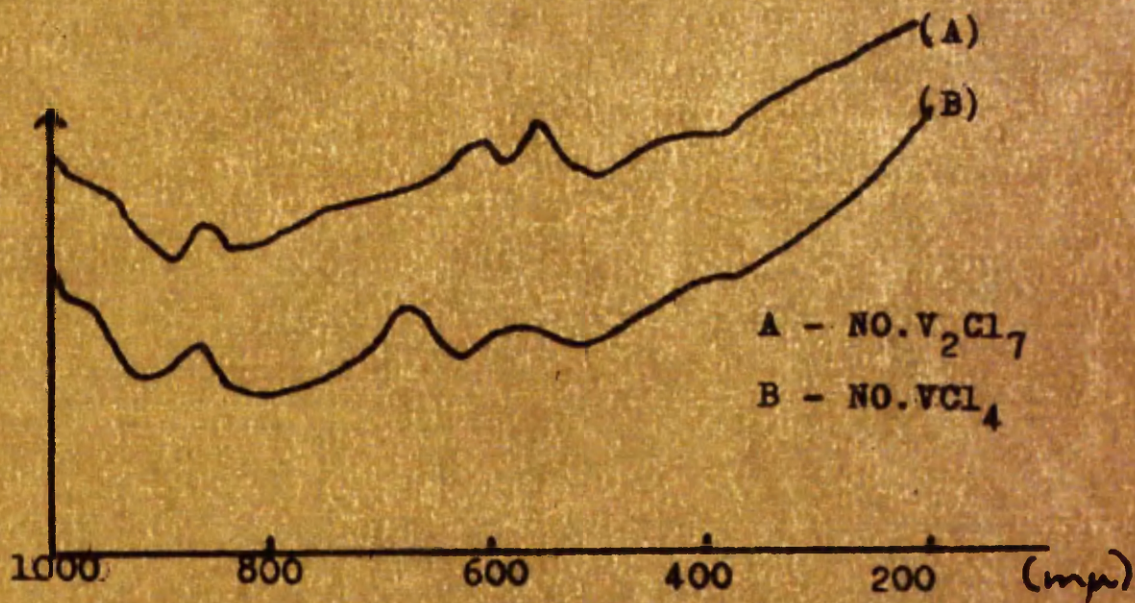
Reflectance spectra were run on a Milger-Watts Uvispek Photoelectric Spectrophotometer Model H700 307, between the limits 200 mμ and 1000 mμ .

Infra-red spectra were run on a Grubb Parsons DB1 Spectrophotometer. In the cases of $NO.VCl_4$, $NO.V_2Cl_7$, $NO.NbCl_6$, $NO.NbF_6$, $NO.TaCl_6$ and $NO.TaF_6$ the observed nitrosonium ion bands were calibrated against a polystyrene spectrum.

In instances where reaction with a nujol mull was not rapid, nujol was used as the mulling agent. In all other cases, and invariably for calibrated peaks, florube was used.

Reflectance Spectra of Vanadium (III) Complexes





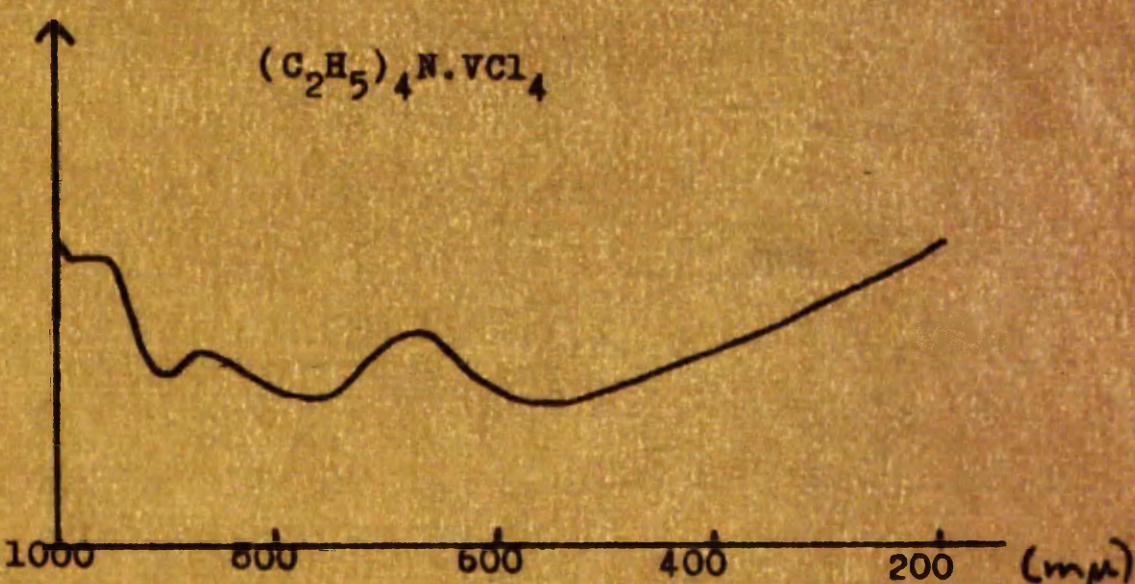


TABLE 1

Calculated Values for tetrahedral d^2 system. ($Dq = -500\ cm^{-1}$) (Liehr & Ballhausen 1959)		V^{3+} in $CSAlCl_4$ host lattice (Gruen & Gut 1961)	$NO.VCl_4$
625 m	$^3T_1$	667 m	420-430 m (sh.)
1110 m		985 m	580 m
2000 m	$^3T_2$	1064 m	670 m
		1212 m	870 m
			960 m

$(C_2H_5)_4N\ VCl_4$	$NO.V_2Cl_7$
	940 m
675 m	865 m
870 m	750 m
955 m	620 m
	570 m
	490 m (Sh.)

CHAPTER VI

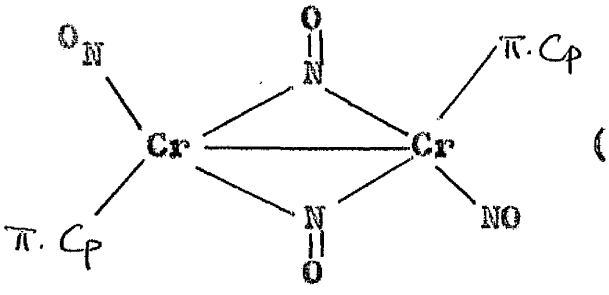
CHROMIUM AND MOLYBDENUM

Although a number of compounds containing chromium or molybdenum - nitric oxide bonds are known, very little is known of the behaviour of compounds of molybdenum and chromium in nitrating and nitrosylating solvents.

Chromium-nitrosonium ion bonds have been characterised by infrared spectroscopy in a series of covalent compounds of the general formula $(NO)_2Cr(\pi\text{-}C_5H_5).X$ where X = -Cl - Br - SCN - CH_3 - C_2H_5 - CH_2Cl - $.C_5H_5$ - C_6H_5. (Lewis et al 1958). The same diagnostic method also characterised the $Cr\text{-}NO^+$ bond in the complex anion $[Cr(CN)_5NO]^{3-}$ (Hieber & Jahn 1958).

The complex cation $[Cr(H_2O)_5\ NO]^{+}$ is postulated as containing $Cr^{2+} \leftarrow NO^-$ linkages (Ardon & Herman 1962).

Terminal and bridging nitrosonium ion ligands are believed to be present in the binuclear complex:-



(King & Bisnette 1964)

Infrared spectroscopy has been used to characterise the molybdenum - nitrosonium ion bond in the covalent species $(NO).Mo(CO)_2.(\pi.C_5H_5)$, (Lewis et al 1958) and in the anionic species $Mo(CN)_5NO^{3-}$ (Hieber & Jahn 1958).

Nitrosonium salts of fluoro-acids of molybdenum, tungsten and uranium have been prepared (Geichmann et al 1962, 1963; Seel & Birnkraut 1962) and have been discussed in chapter I. Seel & Birnkraut prepared $NO.MoF_6$, $NO.WF_7$ and $NO.UF_6$ using the metallic elements and the reagant $NOF(HF)_3$; attempts, using the same reagent, to obtain nitrosonium fluorochromates were unsuccessful, the only products being chromium(III) fluoride.

In the present work, the behaviour of chromic and chromous chlorides with nitrosyl chloride and dinitrogen tetroxide was observed, and this was partially extended to chromium oxides and oxychlorides. Molybdenum was covered in an analogous manner.

REACTIONS OF NITROSYL CHLORIDE WITH CHROMOUS AND CHROMIC CHLORIDE.

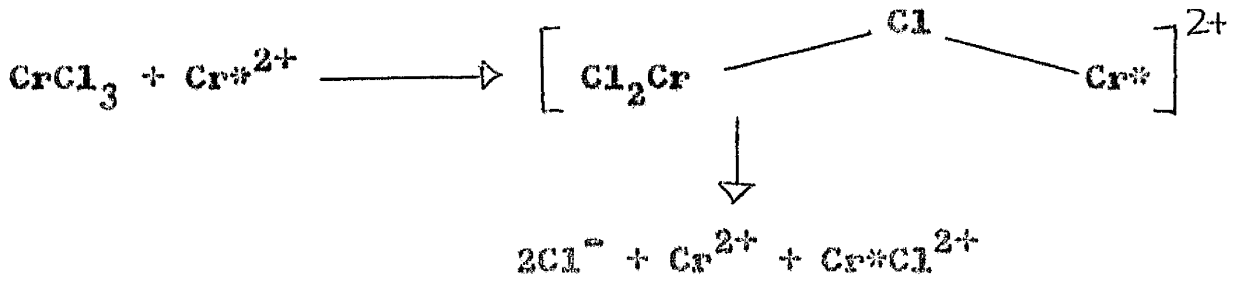
Chromic chloride will not react with nitrosyl chloride, even after shaking for 2 - 3 weeks, or on heating up to 100°C; chromous chloride reacts almost instantaneously with liquid nitrosyl chloride to give a

yellow product $(NO)_3Cr_2Cl_9$, which contains only Chromium (III).

When a trace (i.e. c. 1%) of chromous chloride is added to chromic chloride the resultant mixture will react very readily with liquid nitrosyl chloride to give the same product $(NO)_3Cr_2Cl_9$.

This ability of chromous chloride to activate reactions involving chromic chloride is well known; the commonest example of this being the behaviour of chromic chloride in water. In the absence of chromous chloride, chromic chloride is highly insoluble in water, but in the presence of a trace of the chromous salt(Sidgwick (1950) quotes the ratio 1 part in 40,000), chromic chloride dissolves readily and crystallises out as the hexahydrate. The ability of other reducing agents, such as ferrous and stannans chlorides, to similarly activate the dissolution of chromic chloride was observed by Drucker as early as 1901.

Taube and Myers (1954) studied the activation of chromic chloride and chromic iodide and the chlorochromate (III) $CrCl^{2+}$ anion by chromous chloride, and in all of these cases postulated the formation of an activated binuclear complex with a halogen bridge, viz:-



Hence chromium (III) passes into solution as the $CrCl^{2+}$ species, and Taube and Myers also cite evidence that the retained chlorine in this cation did not pass through the solution. Hence the most reasonable mechanism is atom-transfer via a bridged complex.

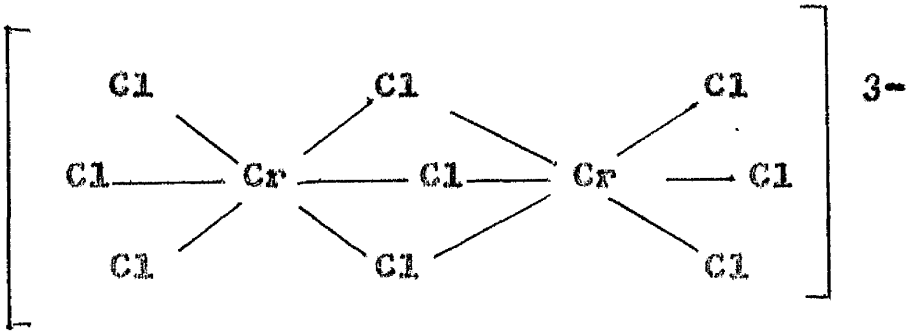
It is very probable that the same type of mechanism is responsible for the behaviour of chromous/chromic mixtures in nitrosyl chloride.

The compound $(NO)_3Cr_2Cl_9$ gives one prominent infrared absorption band at 2229 cm^{-1}. This is in the free nitrosonium ion absorption region, and the absence of other bands indicates that all the nitric oxide groups are present as nitrosonium ions. Hence the compounds must be formulated $(NO^+)_3 \quad (Cr_2Cl_9^{3-})$.

The $Cr_2Cl_9^{3-}$ anion has been characterised in the compound $Cs_3Cr_2Cl_9$ (Wessel & Ijdo 1957).

Complex chlorides of this type are built up from a close-packed halogen lattice with cations, in this instance caesium ions, fitting into lattice holes, and chromium ions fitting into certain pairs of octahedral

holes to maintain the stoichelometry. Hence each chromium ion is octahedrally surrounded by six chloride ions and the structure of the anion is thus one of two $CrCl_6$ octahedra linked across a face, i.e. there are three bridging chlorine atoms, Viz:-



The chromium (III) ion has a d^3 external configuration, and hence gives rise to a characteristic ultraviolet spectrum, in the presence of a perturbing electrostatic field, i.e. in a ligand field.

The spectrum of chromic chloride, $CrCl_3$, and the $(Cr_2Cl_9)^{3-}$ anion should be fairly similar, since in both cases the chromium ion is in an octahedral field of six chloride ions. Differences may arise in the two instances due to:-

a) In the $Cr_2Cl_9^{3-}$ anion, Cr - Cl - Cr bridging may distort the symmetry of the $CrCl_6$ units from the perfect octahedral structure. Since this type of bridging will be absent in chromic chloride, the chromium ion in this latter instance will be in a more regular octahedral environment.

b) Distortions of the $Cr_2Cl_9^{3-}$ anion enforced by the crystal lattice in which it is set; such distortions could remove the symmetry of the anion and give use to band splittings.

The ultraviolet and visible spectra of $(NO)_3\ Cr_2Cl_9$ and $\left[(C_2H_5)_4N\right]_3Cr_2Cl_9$ are given; in addition, the main bands are tabulated (table 1), together with those given in the literature for chromic chloride (Jorgensen 1962).

The tetraethyl ammonium salt was prepared by the following metathetical reaction in liquid sulphur dioxide:-

$$3(C_2H_5)_4N.Cl + (NO)_3Cr_2Cl_9 \longrightarrow \left[(C_2H_5)_4N\right]_3Cr_2Cl_9 + 3NOCl$$

$\left[(C_2H_5)_4N\right]_3Cr_2Cl_9$ separated out as a red-brown solid.

The visible and ultraviolet spectra of chromium (III) complexes are best understood from a consideration of the energy levels of a d^3 ion in a ligand field (see diagram).

In chromic chloride the main bands are assigned as shown in table 1 (Jorgensen, 1962, pp.290 - 291). By comparison, the $^4T_2 \longrightarrow {}^4A_2$ transition in $\left[(C_2H_5)_4N\right]_3 Cr_2Cl_9$ occurs at 720 mμ, and in $(NO)_3Cr_2Cl_9$ it seems likely that the triply split bands centred about 695 mμ are due to this same transition.

The other allowed transition arising from ground state terms, the $^4T_1 \longrightarrow {}^4A_2$ occurs at 529 mμ in chromic chloride. It seems likely that the 490 mμ band in $\left[(C_2H_5)_4N\right]_3 Cr_2Cl_9$ is due to a $^4T_1 \rightarrow {}^4A_2$ transition. The shoulder at 540 mμ in the spectrum of $(NO)_3Cr_2Cl_9$ is likely to be due to a forbidden transition and the strong band at 420 mμ is probably due to the $^4T_1 \rightarrow {}^4A_2$ transition. If this is the case, it is notable that this transition is shifted to significantly higher energies in both instances of the $Cr_2Cl_9^{3-}$ anion, than in chromic chloride.

The weaker bands, in $\left[(C_2H_5)_4N\right]_3Cr_2Cl_9$ and $(NO)_3Cr_2Cl_9$, above 900 mμ may be due to forbidden transitions of the $^2T_1$ or $^2E \rightarrow {}^4A_2$ type.

Consideration of the energy diagram of a d^3 ion enables a tentative assignment of the 540 mμ band in $(NO)_3Cr_2Cl_9$ to be made, to a $^2T_2 \rightarrow {}^4A_2$ transition, which is strictly forbidden.

Thus, the spectroscopic evidence indicates that the $Cr_2Cl_9^{3-}$ anion in both the above instances are based on bridged $CrCl_6$ octahedra but the band splittings and band displacements observed, indicate that significant loss of symmetry has almost certainly occurred.

CHROMOUS AND CHROMIC CHLORIDES/DINITROGEN TETROXIDE.

As with nitrosyl chloride, no reaction occurred between chromic chloride and dinitrogen tetroxide, even when the products were shaken together for several days. The reaction was unaffected by the presence of ionising solvents, such as acetonitrile and nitromethane. This demonstrated that an increase in nitrate ion concentration did not affect the reaction.

The auto-ionisation

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

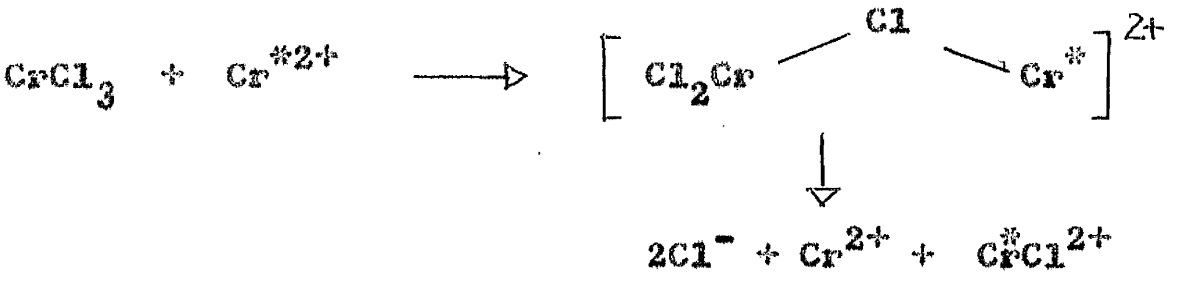
is small, but this would be considerably increased in an ionising solvent, which would probably complex the nitrosonium ion, and thus drive the equilibrium towards the right hand side.

Chromous chloride reacted quite rapidly with liquid dinitrogen tetroxide to give a pale green solid and a green solution. The solid analysed as an adduct of anhydrous chromium nitrate, $Cr(NO_3)_3 \cdot 2N_2O_4$. This has also been reported in the literature as being formed in the chromium hexacarbonyl/dinitrogen tetroxide reaction (Addison & Chapman 1964).

Chromic chloride, with about 5 - 6% chromous chloride, reacts with dinitrogen tetroxide, but much more slowly than with nitrosyl chloride. The reaction product

is, again, the same as in the system involving chromous chloride only, but the reaction in this case requires shaking for 3 - 4 hours at room temperature.

This is understandable, remembering the electron transfer reaction by which chromic ion goes into solution:-



$$CrCl_3 + Cr^{*2+} \longrightarrow \left[Cl_2Cr \overset{Cl}{\diagup\!\diagdown} Cr^{*} \right]^{2+} \longrightarrow 2Cl^- + Cr^{2+} + \overset{*}{Cr}Cl^{2+}$$

i,e. chromic ion goes into solution as the $CrCl^{2+}$ cationic species; this will only marginally affect the reaction rate in the formation of $(NO)_3Cr_2Cl_9$ since there is no necessity to cleave the Cr - Cl bond, as the $(Cr_2Cl_9)^{3-}$ anion only involves Cr - Cl bonding. However, in the reaction involving dinitrogen tetroxide, the situation is different.

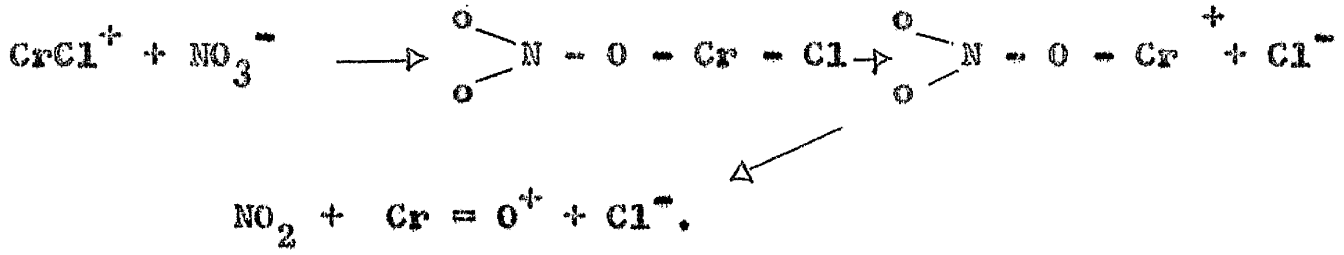
The fast reaction step is probably the 'solubilisation' of chromic ion as the $CrCl^{2+}$ species; the slow reaction step is the substitution reaction of the type:-

$$CrCl^{2+} + N_2O_4 \longrightarrow Cr(NO_3)^{2+} + NOCl$$

$$\text{or} \quad CrCl^{2+} + NO_3^- \longrightarrow Cr(NO_3)^{2+} + Cl^-$$

giving chromium nitrate or nitrato species which will eventually give the product $Cr(NO_3)_3.2N_2O_4$.

The chromous chloride/dinitrogen tetroxide reaction will be different because in this case there are no chromic species to go into solution; the reactant species will be either Cr^{2+} ions or $CrCl^{+}$ ions. If the latter react with nitrate ion from dinitrogen tetroxide autoionisation, it is very likely that an oxidation-reduction reaction will take place, to give chloride-free chromium (III) species viz:-



Naturally this is only a schematic representation, since the chromium is very likely to be more highly co-ordinated that the above mechanism shows.

The infrared spectrum of the $Cr(NO_3)_3.2N_2O_4$ was examined, and its behaviour in Nujol mull found to be highly unusual. In a Florube mull two prominent bands were present at 2336 cm^{-1} and 2278 cm^{-1}, with a further strong band at 1471 cm^{-1}. When the spectrum was run in Nujol mull, the bands at 2336 cm^{-1} and 2278 cm^{-1} disappeared almost completely, even when the spectrum

was run as quickly as possible. A sharp band appeared at 1751 cm^{-1}, and the 1471 cm^{-1} peak seemed to be largely unaffected, though this was difficult to verify as Nujol itself absorbs very strongly at 1460 cm^{-1} and 1377 cm^{-1} approximately, and, in all the spectra of $Cr(NO_3)_3.2N_2O_4$ run in Nujol, a high level of absorption due to the compound was observed in the 1540 - 1330 cm^{-1} region, but the location of band peaks was difficult to ascertain.

It would have been expected that the remainder of the bands in the infrared spectrum of $Cr(NO_3)_3.2N_2O_4$ would show a time-dependence with regard to their relative intensities, such a dependence enabling decomposition product bands to be eliminated. However, this was not the case.

The infrared spectrum in Nujol showed further bands at:-

1297s, 1256m, 1167w, 1012s, 800m, 719s.

The relative intensities of these bands were little affected by time. Hence, either all the bands mentioned above are decomposition bands, or else only the species responsible for the 2336 cm^{-1} and 2278 cm^{-1} bands are affected by Nujol. Provided the Nujol was thoroughly dry, no obvious signs of decomposition were

apparent in $Cr(NO_3)_3.2N_2O_4$/Nujol mulls, even over a period of time, but obviously this is not conclusive; decomposition products of chromium (III) would be expected to be green.

The reflectance spectrum of $Cr(NO_3)_3.2N_2O_4$ was observed the complete time for a run over the 200 mμ - 1000 mμ region was 30 - 40 minutes, and practically no decomposition occurred over this period, if all the components, including the cell and the potassium chloride diluent, were rigorously dried beforehand, and the non-entry of air assured, during the course of the run. The bands in the spectrum of $Cr(NO_3)_3.2N_2O_4$ are tabulated in table 2 . Bands and assignments for the $[Cr(oxalate)_3]^{3-}$ anion (Jorgensen 1962, pp 290 - 291) are tabulated also. In the latter instance, chromium (III) is known to be in an octahedral environment of oxygen atoms, and the same is possible in the case of $Cr(NO_3)_3.2N_2O_4$.

By comparison with the data on the $[Cr(oxalate)_3]^{3-}$ anion, the following assignments can be made for the compound $Cr(NO_3)_3.2N_2O_4$. The strong band at 610 mμ can be assigned to the $^4T_2 \longrightarrow {}^4A_2$ transition, and it seems likely that the shoulder at 680 mμ will be due to the Laporte - forbidden $^2T_1, {}^2E \longrightarrow {}^4A_2$ transition. Unfortunately this means that the broad absorption centred about 900 mμ cannot be characterised.

The higher energy bands are more complicated to assign; it is very probable that one of the bands at 460 mμ or 400 mμ can be assigned to the $^4T_1 \rightarrow {}^4A_2$ transition, in which both terms arise from the ^4F ground state. Since both these bands have intensities of the same order of magnitude, they are both likely to be allowed transitions. It is possible that the $^4T_1$ level has been split due to loss of symmetry, and that both these bands arise from the same transition, $^4T_1 \rightarrow {}^4A_2$.

The band at 320 mμ may be due to the $^4T_1(^4P) \rightarrow {}^4A_2$ transition, but the intensity suggests that a charge-transfer process may be responsible for this band, possibly involving 'adducted' dinitrogen tetroxide.

However, there is sufficient evidence to show that the reflectance spectrum of $Cr(NO_3)_3.2N_2O_4$ can be interpreted in terms of chromium existing in an octahedral environment, probably distorted, and probably of oxygen atoms, though the possibility of some co-ordination via nitrogen cannot be ignored.

If the chromium is six-co-ordinate, and this seems highly probable, the nitrato-groups are most likely to be behaving as bidentate ligands, either bridging or donating to just one chromium ion.

It is not possible to assign a structural formula unambiguously. The infrared data are inconclusive, and

the following possibilities exist:-

$$(NO^+)_2 \cdot (Cr(NO_3)_5)^{2-}$$

or

$$(NO^+) \cdot (Cr(NO_3)_4)^- \cdot N_2O_4.$$

If 'adducted' dinitrogen tetroxide is present as in the latter formulation, it may behave as a ligand, and may possibly donate via the nitrogen-atom.

It seems unlikely, from thermal decomposition studies, that the latter structure is the correct one. Such a structure would be expected to decompose according to the equation

$$(NO^+) \cdot (Cr(NO_3)_4^-) \cdot N_2O_4 \longrightarrow (NO^+) \cdot (Cr(NO_3)_4^-) + 2NO_2.$$

No evidence was found for such a dissociation; the products of thermal decomposition could not be characterised, but seemed to consist largely of chromic oxide Cr_2O_3. No formation of the anhydrous trinitrate, $Cr(NO_3)_3$, occurred by these means, and this is in accord with the observations of Addison & Chapman (1964).

However, chromic trinitrate has been prepared by the latter workers by the reaction of dinitrogen pentoxide with chromium hexacarbonyl; this demonstrates, again, that in general, reaction of a metal compound with

dinitrogen pentoxide affords a better route to the anhydrous metal nitrate, than does reaction with dinitrogen tetroxide.

Addison & Chapman (1964) have shown that chromium trinitrate is a covalent compound, containing co-ordinated nitrato-ligands, on the basis of the infrared spectrum of the compound.

CHROMIUM TRIOXIDE, CrO_3 + NITROSYL CHLORIDE.

Chromium trioxide reacts fairly readily with liquid nitrosyl chloride to give a shiny black crystalline product, analysing as $(NO)_2\ Cr_3O_8Cl$.

It dissolves in water with effervescence to give a yellow-brown solution which contains both Cr(III) and Cr (VI) species. Redox titrations showed that the ratio of the species was Cr(VI) : Cr (III) = 2 : 1, which makes the 'overall' oxidation state of chromium in this compound equal to +5. It is rather unlikely that chromium exists in the +5 oxidation state in the compound $(NO)_2\ Cr_3O_8Cl$, and a mixture of Cr(III) and Cr(VI) is much more likely. In addition, such a structure would explain the intense colour of the compound as being due to Cr(III)—▶Cr(VI) charge transfer reactions.

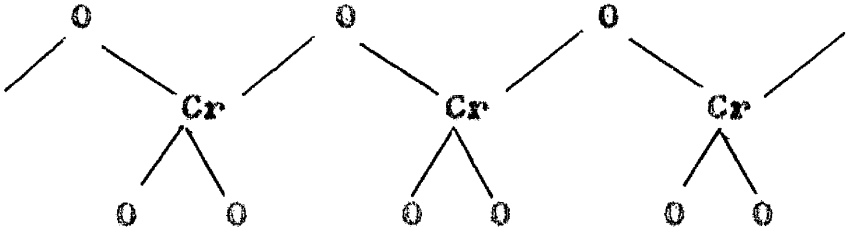
The infrared spectrum of the compound is very simple and the bands are tabulated below, with other

compounds containing chromium-oxygen linkages for comparison.

K_2CrO_4	$K_2Cr_2O_7$	CrO_3	CrO_2Cl_2	$(NO)_2Cr_3O_8Cl$
		all values in cm^{-1}		
885s	934s	965s	1026s	2340m
850m	900s	890m	909m	964s
	878s		847s	887m
	746 broad,vs		820-794 split,s.	

In $(NO)_2Cr_3O_8Cl$, the band at 2340 cm^{-1} is indicative of free nitrosonium ion, and the absence of bands in the 1600-2000 cm^{-1} region shows that metal - nitrosonium ion bonding does not occur.

The lower frequency bonds in the infrared spectrum of $(NO)_2Cr_3O_8Cl$ show a marked similarity to chromium trioxide, CrO_3, which consists structurally of linked CrO_4 tetrahedra (Bystrom & Wilhelmi 1950), viz:-



hence it seems probable that $(NO)_2Cr_3O_8Cl$ incorporates Cr(VI) in this type of environment, with the Cr(VI)O4

units having C_{2v} symmetry.

K_2CrO_4 contains discrete $[CrO_4]^{2-}$ tetrahedra (Zachariasen & Ziegler, 1931) and $K_2Cr_2O_7$ contains the $Cr_2O_7^{2-}$ anion, which consists of two CrO_4 tetrahedra linked via one corner (Bystrom & Wilhelmi 1951).

Hence it can be inferred from the infrared data that in $(NO)_2Cr_3O_8Cl$, CrO_4 units are doubly linked, either to one another as in chromium trioxide, or to other units.

Reflectance data on $(NO)_2Cr_3O_8Cl$ gave bands in the following regions:-

760 mμ	Sh, w	
710 "	w	
570 "	Sh, m	
350 "	s	(See also Diagram 4)

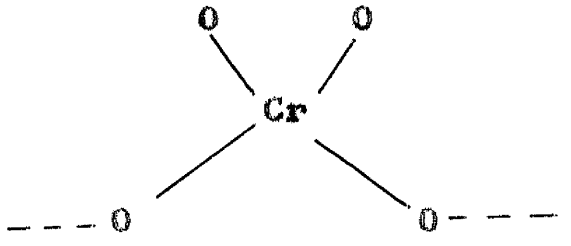
The band at 710 mμ is characteristic of Cr(III) in an octahedral environment. This band presumably is weak because Cr(III) is in a 'dilute' state in the compound.

Diagram 4 shows that the intensity of absorption increases with decrease in wavelength (increasing energy), and it is likely that this increase is due to charge-transfer reactions between Cr(III) and Cr(VI). A black compound K Cr_3O_8 is known. It has been shown to contain tetrahedrally co-ordinated Cr(VI) and octahedrally co-ordinated Cr(III). These $Cr(VI)O_4$ and $Cr(III)O_6$ units link together to form layers of composition Cr_3O_8 in which

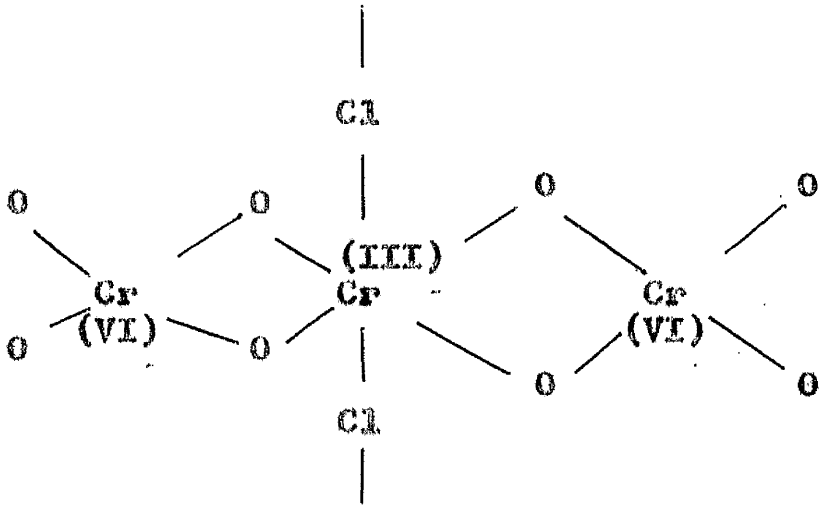
the ratio Cr(VI) : Cr(III) is equal to 2 : 1. These layers are held by potassium ions (Wilhelmi, 1958).

In KCr_3O_8, the anion is thus polymeric, $[Cr_3O_8]_n^{n-}$, and n probably has a very large value.

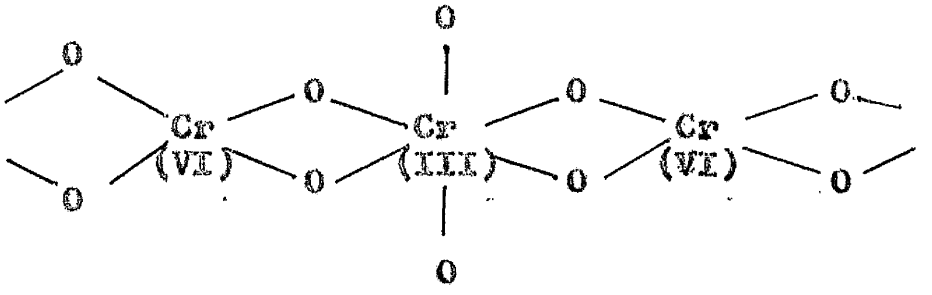
The anion $Cr_3O_8Cl^{2-}$ could consist of Cl^- and $Cr_3O_8^-$ anions, with the latter having the same structure as in KCr_3O_8. Alternatively, $Cr_3O_8Cl^{2-}$ units may exist which would give rise to polymeric structures. Assuming octahedrally co-ordinate Cr(III) and tetrahedrally co-ordinate Cr(VI) it is not possible to construct a satisfactory monomeric $Cr_3O_8Cl^{2-}$ anion. Also, the infrared evidence suggests that the symmetry of the $Cr(VI)O_4$ units is similar to that in chromium trioxide, i.e. the units link to two other units via two oxygen atoms:-



Such considerations probably necessitate a structure of the type shown below, involving bridging oxygen and chlorine atoms, viz:-



The chlorine atoms bridge between Cr_3O_8 units. This compares with the structure of the $Cr_3O_8^-$ layers in KCr_3O_8:-



(Wilhelmi 1958).

In the latter instance, Cr - O - Cr bridging causes polyanion formation along the same axis as the chromium ions; in the former instance, Cr - Cl - Cr bridging causes polyanion formation perpendicular to the plane of the chromium ions, but it is apparent from the diagrams that such structures are closely related.

However, distinction between the $Cr_3O_8Cl^{2-}$ and $Cr_3O_8^- + Cl^-$ types of structure would require a full crystallographic study.

Since the compound KCr_3O_8 is known, it was thought to be of interest to heat $(NO)_2Cr_3O_8Cl$ to attempt to bring about the reaction:-

$$(NO)_2Cr_3O_8Cl \longrightarrow NO.Cr_3O_8 + NOCl.$$

i.e. to attempt to obtain the nitrosonium analogue of KCr_3O_8. On heating to 200°C, nitrosyl chloride was evolved, together with nitrogen dioxide; a blackish-green residue remained which seemed to be a mixture of Cr_2O_3 and CrO_2. It appears that a redox reaction probably occurred between nitrosonium ion and chromium (VI). There was no evidence for the formation of $NO.Cr_3O_8$; nitrosyl chloride and nitrogen dioxide were evolved simultaneously.

This reaction is similar in some respects to the Vanadium pentoxide/nitrosyl chloride reaction mentioned in the last chapter. Unfortunately a proper comparison is not possible since the products were not identified in the latter case, but it is apparent that in both instances the nitrosyl chloride has behaved as a reducing agent.

CHROMIUM TRIOXIDE/DINITROGEN TETROXIDE.

Chromium trioxide will dissolve very slightly in dinitrogen tetroxide to give a green solution; the extent of solution seems to be greater than with vanadium

pentoxide and dinitrogen tetroxide.

It was hoped that formation of $CrO_2(NO_3)_2$ species might occur, but gas phase spectra indicated only the presence of nitrogen dioxide, and no information about the dissolved species was obtained. No solid product was formed and the solid residue consisted entirely of chromium trioxide.

It is possible that the conditions were not vigorous enough for reaction to occur, Gibson & Katz (1951) hav e carried out the reaction between uranium trioxide and dinitrogen tetroxide, at 90°C and under a pressure of 14.5 atmospheres of the latter, to obtain $UO_2(NO_3)_2 \cdot N_2O_4$.

Chromyl nitrate, $Cr_2(NO_3)_2$, has been prepared by the reaction of chromyl chloride or chromium trioxide with dinitrogen pentoxide:-

$$CrO_3 + N_2O_5 \longrightarrow CrO_2(NO_3)_2$$

$$CrO_2Cl_2 + 2N_2O_5 \longrightarrow CrO_2(NO_3)_2 + 2NO_2Cl$$

(Schmeisser & Lutzow, 1954)

It was obtained as a volatile red liquid and thus is most likely to exist as monomeric species at room temperature, with the nitrate groups behaving as unidentate ligands. This contrasts strongly with $UO_2(NO_3)_2$, which is a solid

(Gibson & Katz 1951, Gibson et al 1960, Addison et al 1964), and may contain the UO_2^{2+} cation (Addison et al 1964).

No examples are known of the free chromyl cation CrO_2^{2+}.

CHROMYL CHLORIDE:

REACTIONS WITH NITROSYL CHLORIDE AND DINITROGEN TETROXIDE.

These reactions have not been fully investigated, and merit further study. The reaction CrO_2Cl_2/N_2O_4 was hoped to yield chromyl nitrate, thus:-

$$CrO_2Cl_2 + 2N_2O_4 \longrightarrow CrO_2(NO_3)_2 + 2NOCl \qquad 1$$

A very small quantity of a blue-green solid was recovered; gas phase spectra indicated that only a mixture of nitrogen dioxide and nitrosyl chloride was present, thus showing that some reaction had occurred, but there was no evidence for the formation of nitrato-ligands or chromyl groups.

However the presence of nitrosyl chloride does suggest an initial reaction of type 1 , above, but if chromyl nitrate was formed, further reaction could occur between

a) $CrO_2(NO_3)2$ and N_2O_4, towards adduct formation.

b) CrO_2Cl_2 and the NOCl formed.

The reaction between chromyl chloride and nitrosyl chloride yielded a very small quantity of a bright green solid; as with the CrO_2Cl_2/N_2O_4 reaction product, no analysis was possible. The colour definitely suggests that reduction of chromium (VI) has occurred. In both these instances, the infrared spectra of the reaction products are identical, thus two effects could have occurred:-

a) The two reactions could yield largely identical products, due to favourable secondary reactions occurring in one of the instances.

b) Reaction could have occurred in Nujol mull, thus making most of the bands decomposition bands.

The latter possibility does seem rather unlikely, since even in florube, which is highly unreactive, both products gave identical spectra.

It is very probable that reduction of chromium (VI) occurs in the main reaction but the oxidation state which chromium finally attains is not known.

ATTEMPTED REACTION

INVOLVING METALLIC CHROMIUM.

The reaction between vanadium and dinitrogen tetroxide in acetonitrile solution to give VO_2NO_3 (Pantonin et al 1960) has been mentioned in the previous chapter.

When the analogous chromium reaction was attempted, no reaction occurred either in pure dinitrogen tetroxide or with ionising solvents, e.g. nitromethane and acetonitrile.

MOLYBDENUM

The trend towards enhanced stability of higher oxidation states with increasing atomic number, as observed in the vanadium-niobium-tantalum series, is repeated in the chromium-molybdenum-tungsten series. The oxidation states +3 and +6 are particularly well characterised in chromium, and this is also the case with molybdenum. However, with the latter the +4 and +5 oxidation states are much better known, both as halides and oxyhalides and in complex anions.

As has been pointed out, systems are known in which molybdenum-nitrosonium covalent bonds exist, both in purely covalent species such as $NO.Mo.(CO)_2(\pi\text{-}C_5H_5)$ and anionic species such as $(Mo(CN)_5NO)^{3-}$.

The nitrosonium salts $NO.MoF_6$ (Geichmann et al 1963; Seel & Birkkvant 1962) and $NO.MoF_7$ (Geichmann et al 1963) are known. The latter workers have also obtained the nitronium salt $NO_2.MoF_7$. Apart from this, no other nitrosonium or nitronium halomolybdates have been reported in the literature.

In addition, little work has been reported regarding nitrates and complex nitrates of molybdenum and tungsten, although the data on chemistry of uranyl nitrate are much better covered, and has been reviewed (Comyns 1960). The infrared spectrum of the uranyl nitrate hydrates have been examined (Gatehouse & Comyns 1958).

The present work covers the behaviour of molybdenum chlorides in nitrosyl chloride; to a more limited extent, the behaviour in dinitrogen tetroxide solution is examined.

MOLYBDENUM TRICHLORIDE/NITROSYL CHLORIDE.

Molybdenum trichloride reacts with liquid nitrosyl chloride to give a mixture of products; these were identified as molybdenum tetrachloride $MoCl_4$, and a deep purple, volatile solid of the formula $(NO)_3\ Mo_3\ Cl_{10}$. They were conveniently separated by vacuum sublimation; the gas phase spectra gave no evidence of volatile molybdenum-nitrosonium species.

$(NO)_3\ Mo_3Cl_{10}$

This compound is very deep purple; it is volatile, subliming in vacuo at 90°-93°C. It bears no resemblance to the compound $(NO)_3Cr_2Cl_9$, except that it is a polymeric species.

The infrared spectrum is very simple; a sharp, strong bond is present at 2175 cm^{-1}, with a weak decomposition band at 1802 cm^{-1}. In the spectrum observed in a Nujol mull, a further band is observed at 1000 cm^{-1}.

The 2175 cm^{-1} band is definitely due to the free nitrosonium ion, NO^{+}, and the 1802 cm^{-1} will be due to formation of nitrosyl chloride; the N-O bond in the latter absorbs at 1799 cm^{-1} (Burns & Burnstein 1950).

It was possible that the 1000 cm^{-1} band could be due to a molybdenum-nitrosyl anion structure; the nitrosyl group in such a system is known to absorb in the 1050-1200 cm^{-1} region. However, it is more likely that this is due to molybdenum - oxygen bond formation by reaction of the complex with Nujol. Chromium-oxygen bond frequencies fall in the range 890 cm^{-1} - 1020 cm^{-1}, depending on the bond multiplicity, and the antisymmetric stretching frequency of the uranyl UO_2^{2+} cation appears at 930 cm^{-1} (Gatehouse & Comyns 1958); hence it is likely that molybdenum-oxygen multiple bonds will appear in the 900-1000 cm^{-1} region.

The compound $(NO)_3Mo_3Cl_{10}$ is extremely hygroscopic, but can be handled in the dry-box fairly readily. It is like the vanadium compounds $NOVCl_4$ and NOV_2Cl_7 in this respect.

The absence of bands in the 1600 - 1900 cm^{-1} infrared region implies that all the nitrosonium ions must be unco-ordinated. Hence the compound becomes $(NO^{+})_3\ (Mo_3Cl_{10}^{3-})$. It does seem surprising that a compound with such a high molecular weight should be volatile, but it may sublime with dissociation and structure change; this possibility has been discussed with respect to the compounds $NO.VCl_4$ and $NO.V_2Cl_7$ in the previous chapter.

The above formula $(NO^{+})_3(Mo_3Cl_{10}^{3-})$ necessitates molybdenum being present in more than one oxidation state; since the three molybdenum atoms in each anion have a total oxidation state of +7, it seems most reasonable that molybdenum +2 and +3 should be present, in the ratio:-

molybdenum (II) : molybdenum (III) = 2 : 1

Both molybdenum (II) and molybdenum (III) have incomplete outer electron orbitals, the external configuration of Mo(II) is $4d^4$, that of Mo(III) is $4d^3$; hence they should give rise to characteristic d-d absorption spectra. The available spectroscopic data in the literature cover only molybdenum (III) (Hartmann 1957; Jorgensen 1959.) in anionic species such as the octahedral $MoCl_6^{3-}$ and $MoCl_5(H_2O)^{2-}$. Molybdenum (III) has an external d^3 electronic configuration, and hence will give rise to

a similar energy level diagram to chromium (III); however since molybdenum is in the second transition series, it gives rise to a higher Dq value than does chromium (Jorgensen, 1962, p.114), so that for the same ligand the two cations Cr(III) and Mo(III) will yield different Dq values. Hence, although the energy diagrams are similar, the magnitude of transition energies may differ, and this is observed. In chromium (III), the forbidden $^2T_2 \longrightarrow {}^4A_2$ transition is of similar energy to the $^4T_2 \longrightarrow {}^4A_2$ transition, while in molybdenum (III), the latter occurs at a much higher energy; this is consistent with molybdenum (III) having a higher Dq value.

The reflectance spectrum of $(NO)_3 Mo_3 Cl_{10}$ was observed; the spectrum is shown (Diagram 5), and the main bands are tabulated in table 3 with the data for the $MoCl_6^{3-}$ anion for comparison.

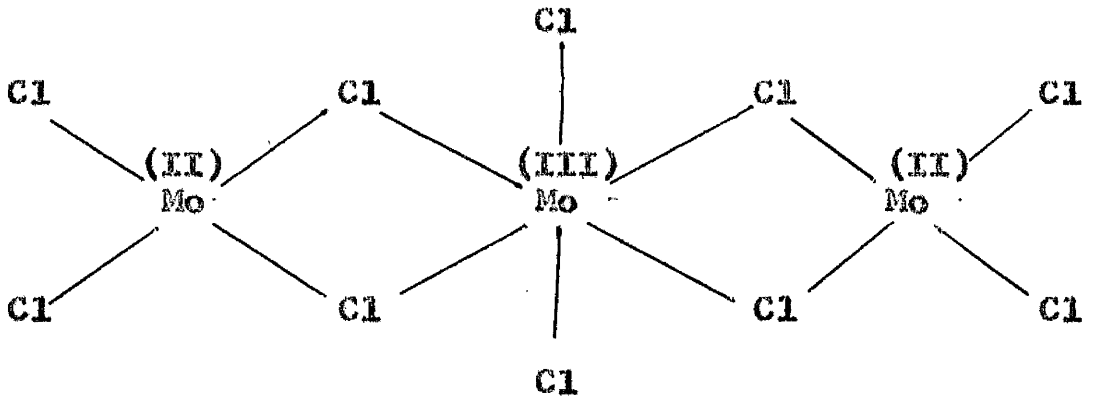
It will be seen that the spectrum of $(NO)_3Mo_3Cl_{10}$ is fairly consistent with the presence of octahedral $MoCl_6^{3-}$ units, especially with regard to the bands at 680 mμ and 425 mμ. By comparison with the data for the $MoCl_6^{3-}$ anion these can be assigned to the $^4T_1 \longrightarrow {}^4A_2$ and $^4T_2 \longrightarrow {}^4A_2$ transitions respectively.

The other bands may be due to the molybdenum (II) ion, for which no literature data could be found; it is unknown in the monomeric state.

Attempts to observe the reflectance spectrum of molybdenum tetrachloride were unsuccessful because of the tendency of this compound to oxidise, even in dry conditions, to give molybdenum (V) species.

However, the available data does suggest the presence of octahedral $MoCl_6^{3-}$ units. The intense blue-violet colour of the compound could be due to charge transfer reactions between molybdenum (II) and (III) species.

If the anion is monomeric $\left[Mo_3Cl_{10}\right]^{3-}$, its structure may be:-



which gives rise to octahedrally co-ordinated molybdenum (III), and four co-ordinate molybdenum (II) species. A more highly polymeric constitution would occur with further chlorine bridging from the $Mo(II)Cl_4$ units, and an increase in co-ordination number of the Mo(II) ion.

When the reaction between molybdenum trichloride and nitrosyl chloride is stopped at an intermediate stage, the product isolated is mainly molybdenum tetrachloride.

This suggests that the primary reaction is of the type:-

$$MoCl_3 + NOCl \longrightarrow MoCl_4 + NO$$

which may occur via an unstable intermediate $NO.MoCl_4$ the nitric oxide thus formed may give species such as $NO.MoCl_3$, thus:-

$$NO + MoCl_3 \longrightarrow NO.MoCl_3$$

and reaction of $NO.MoCl_4$ and $NO.MoCl_3$ species could occur:-

$$2\ NO.MoCl_3 + NO.MoCl_4 \longrightarrow (NO)_3\ Mo_3\ Cl_{10}$$

if such a mechanism is correct, the formation of the complex species is dependent on initial formation of nitric oxide.

Alternatively, the reaction could proceed from a primary disproportionation of the type:-

$$2\ MoCl_3 \rightleftharpoons MoCl_4 + MoCl_2$$

with molybdenum tetrachloride precipitating out, and the monomeric $MoCl_2$ species reacting as above with nitrosyl chloride.

MOLYBDENUM DICHLORIDE/NITROSYL CHLORIDE.

No reaction occurred between these components. This is understandable since the species present in molybdenum dichloride are $[Mo_6Cl_8]^{4+}$ cations and Cl^- anions.

The structure of the former involves considerable metal-metal bonding, as well as metal-chloride bonding. It is thus a very stable unit and difficult to disrupt.

Similarly, no reaction occurred with dinitrogen tetroxide.

Molybdenum Trichloride/Dinitrogen Tetroxide.

Molybdenum trichloride reacts steadily with dinitrogen tetroxide to yield a very pale green solid $MoO(NO_3)_3$; this compound is insoluble in water, and fairly stable to heat, decomposition starting at 130° - 140°C in vacuo.

Only the one solid product was observed from this reaction, although gas phase spectra of the volatile residues at the end of the reaction indicated that nitrosyl chloride was present, no molybdenum tetrachloride or molybdenum nitrosyl chlorides were present. It will be seen that the product, unlike the products from many other dinitrogen tetroxide solvolysis reactions, is not an adduct or a nitrosonium salt. Its inactivity towards water

verifies the latter statement.

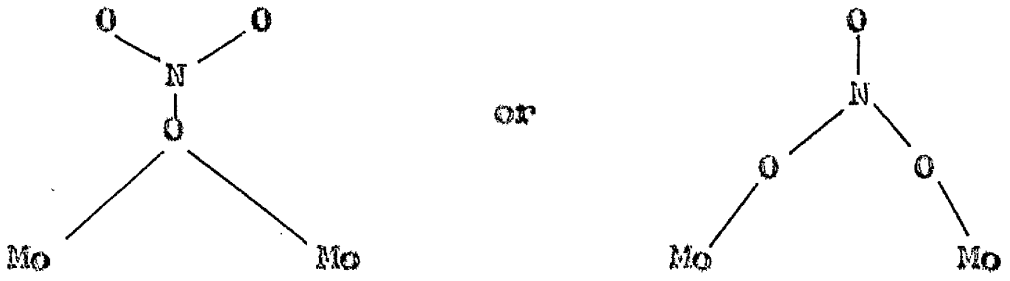
The infrared spectrum shows only a weak absorption in the 2200-2400 cm^{-1} region, and it appears that this absorption is due to a combinational or overtone mode. The intensity of this absorption is independent of the mulling agent used, this is contrary to the behaviour of the compound $Cr(NO_3)_3 \cdot 2N_2O_4$.

The infrared spectrum gave bonds as follows, with assignments:-

3378 w.	-	
2336 w. 2304 w.		(V_3 or $V_5 + V_4$)- nitrato group (split).
1597 m.	-	V_4 - nitrato group
1408 w.	-	$2v_3$ or $2v_5$ nitrato group
1299 m.	-	V_1 nitrato-group
1149 w.	-	
1017 w.	-	
974 s.	-	V_2 nitrato group
917 vs.	-	Mo-O bond stretching mode
800 w.	-	V_6 - nitrato group
719 vs.	-	V_3, V_5 - nitrato group

These bands can be assigned fairly satisfactorily on the basis of a structure involving co-ordinated nitrato-groups and molybdenum-oxygen multiple bonding, as shown; the (V_4-V_1) splitting is 298 cm^{-1} indicating a high degree of covalent bonding.

The structure may be monomeric, but it is more likely that it is polymeric as has been suggested for niobium oxytrinitrate (Field & Hardy 1963,a), with a structure that may involve nitrato-groups acting as bridging ligands, viz:-



Assuming that in the above systems the nitrato-groups are planar, they will both have the same symmetry (C_{2v}) and will thus be indistinguishable from their infrared spectra.

The reflectance spectrum of $MoO(NO_3)_3$ was observed and compared with that for ammonium pentachloro-oxymolybdate $(NH_4)_2 \cdot MoOCl_5$ (Gray & Hare 1962). There is little similarity between the two sets of data, but this could mean that in $MoO(NO_3)_3$, the molybdenum ions are not six co-ordinate, and hence the energy diagrams of the two species will be considerably different.

From a comparison of reflectance data for $MoO(NO_3)_3$ with that for molybdenum (III) species (diagrams 5 and 6), the reflectance data suggest that the

compound contains molybdenum (III) species, but the analytical data do not support this.

The reaction steps were probably of the type:-

$$MoCl_3 + 3N_2O_4 \longrightarrow Mo(NO_3)_3 + 3NOCl$$

The $Mo(NO_3)_3$ could then decompose in two ways:-

$$Mo(NO_3)_3 \longrightarrow MoO(NO_3) + N_2O_5. \text{ (or } N_2O_4 + {}^1/_2\ O_2)$$

$$Mo(NO_3)_3 \longrightarrow MoO_2(NO_3) + N_2O_4$$

The molybdenyl species formed would then have to react with dinitrogen tetroxide, effectively abstracting nitrate ion:-

$$MoO(NO_3) + 2N_2O_4 \longrightarrow MoO(NO_3)_3 + 2NO$$

or

$$MoO_2(NO_3) + 2N_2O_4 \longrightarrow MoO(NO_3)_3 + N_2O_3 \text{ (or } NO + NO_2)$$

There appeared to be no tendency for adduct formation of the types:-

$$MoO(NO_3)_3.\ N_2O_4\ ;\ MoO_2(NO_3).N_2O_4;\ MoO(NO_3).N_2O_4$$

It would appear that if such adducts form, they dissociate very readily. Possibly if $MoO(NO_3)_3$ does have a polymeric structure, this will not be conducive to nitrosonium compound formation, and any adducts formed

will be just 'lattice compounds', with the dinitrogen tetroxide easily removed by heat or reduced pressure.

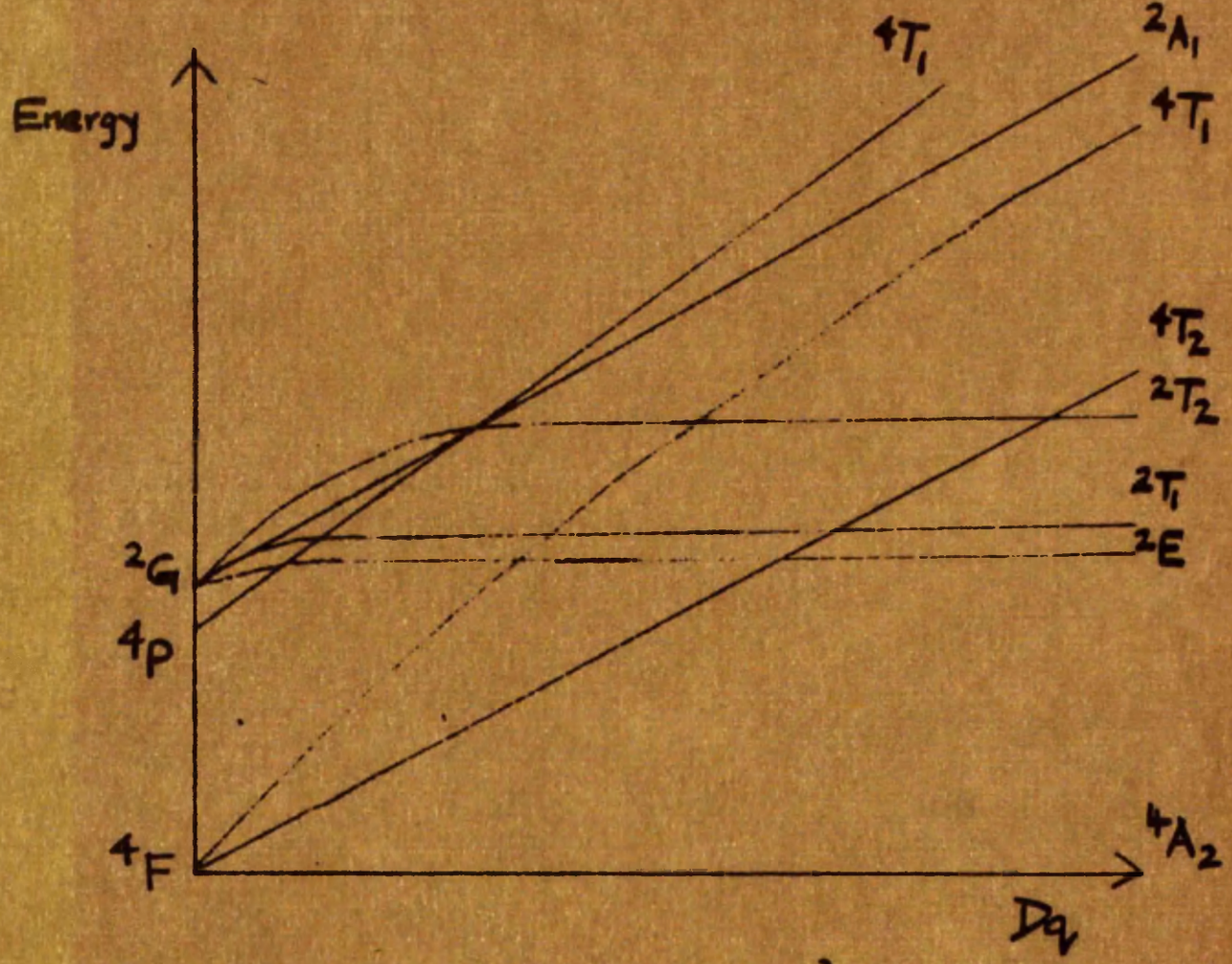
Molybdenum Pentachloride/Nitrosyl Chloride.

These components reacted quite readily to give NO Mo Cl_6; this was a grey powder which hydrolysed very readily in moist air to give dioxymolybdenum dichloride MoO_2Cl_2; in dry air, dissociation into the original components occurred very readily.

The infrared spectrum showed a band, which weakened rapidly with time, at 2180 cm^{-1}, indicating free nitrosonium ion. Hence the compound can be formulated NO^+ $MoCl_6^-$.

The ease of dissociation is similar to that observed with $NO.NbCl_6$; this was discussed in the previous chapter.

The Energy Diagram of a d^3 ion in an Octahedral Field



Chromium (III) has an outer electronic d^3 configuration and in an octahedral electrostatic field, the ^4F ground state gives rise to the $^4A_2$, $^4T_2$ and $^4T_1$ energy terms. The allowed transitions are :-

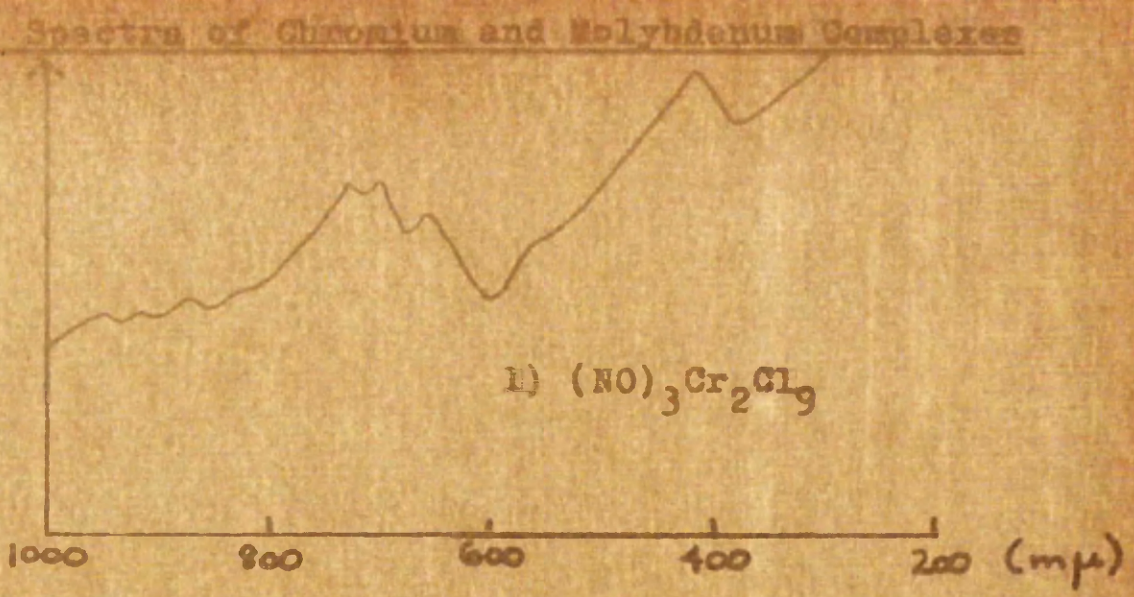
$$^4T_1\ (^4F) \longrightarrow {}^4A_2$$

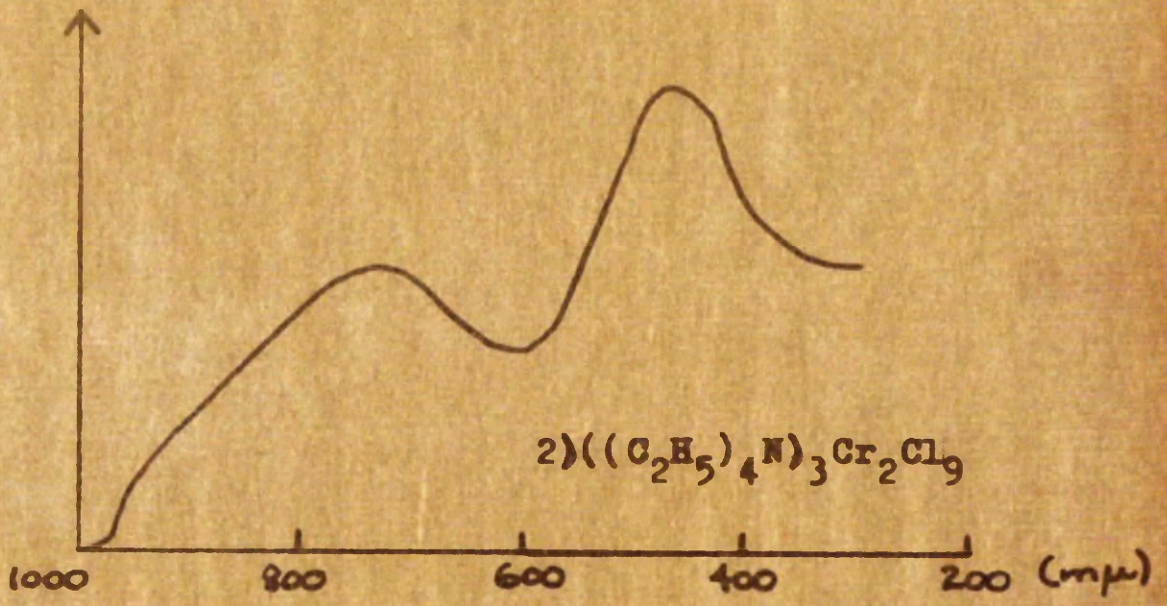
$$^4T_2\ (^4F) \longrightarrow {}^4A_2$$

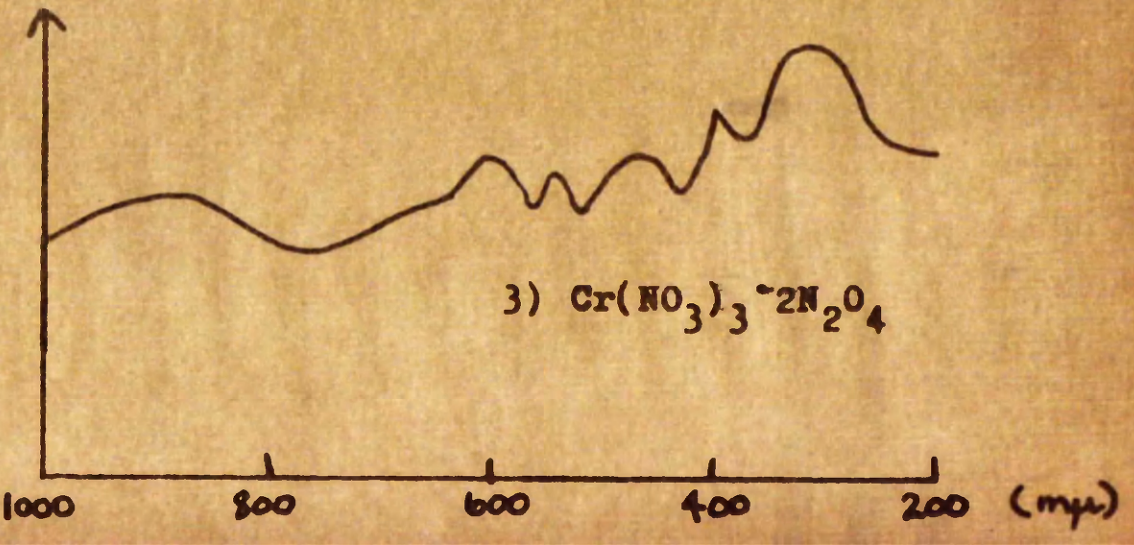
$$^4T_1\ (^4P) \longrightarrow {}^4A_2$$

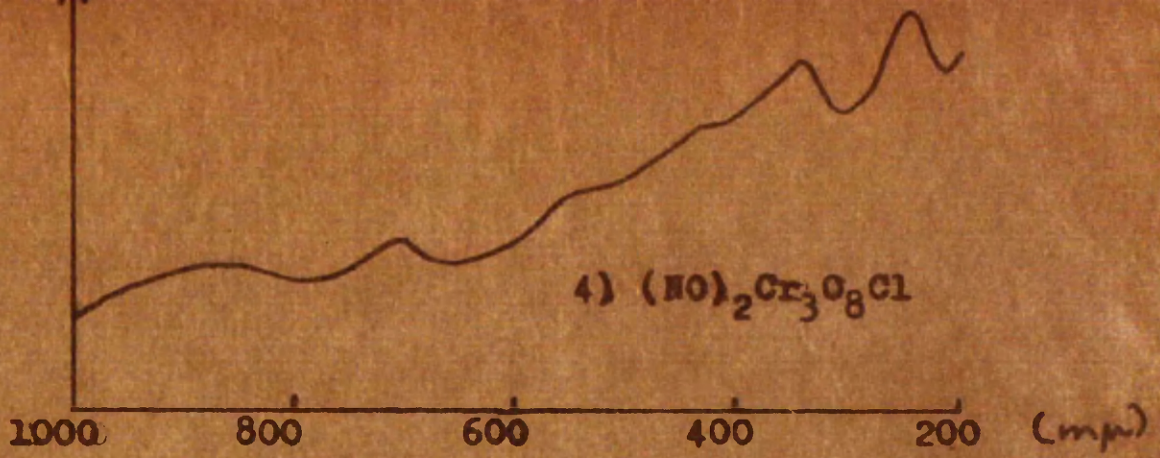
and the following forbidden transitions may occur :-

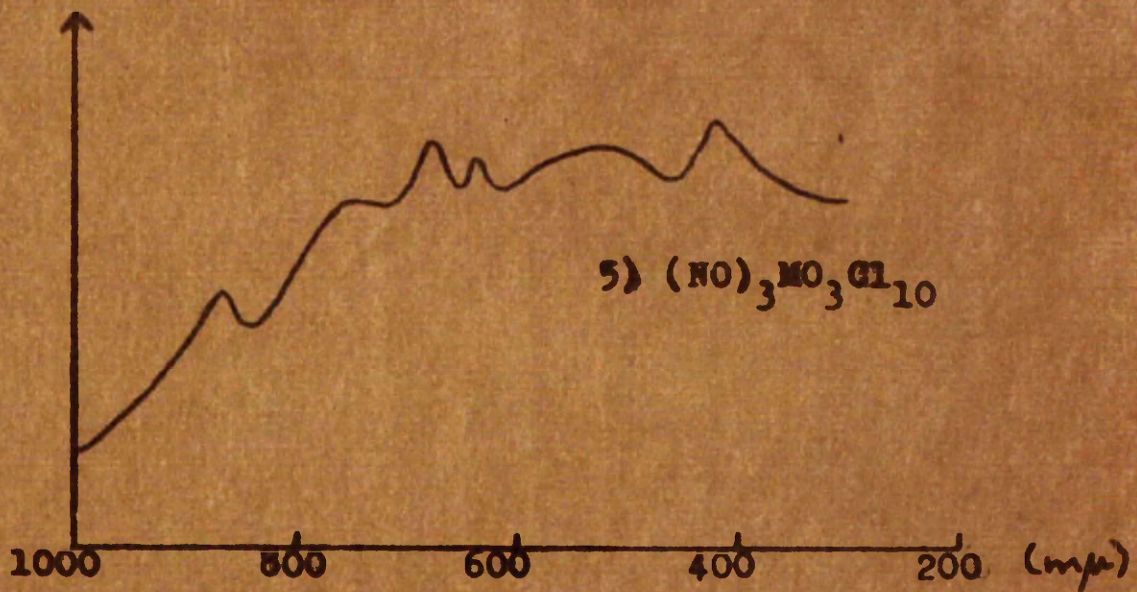
$$^2T_1 \text{ or } {}^2E\ (^2G) \longrightarrow {}^4A_2$$


1) $(NO)_3Cr_2Cl_9$
1000
800
600
400
200 (mμ)


2)$((C_2H_5)_4N)_3Cr_2Cl_9$
1000
800
600
400
200 (mμ)


3) $Cr(NO_3)_3 \cdot 2N_2O_4$
1000
800
600
400
200 (mμ)


4) $(NO)_2Cr_3O_8Cl$
1000
800
600
400
200
(mμ)


5) $(NO)_3MO_3Cl_{10}$
1000
800
600
400
200
(mμ)

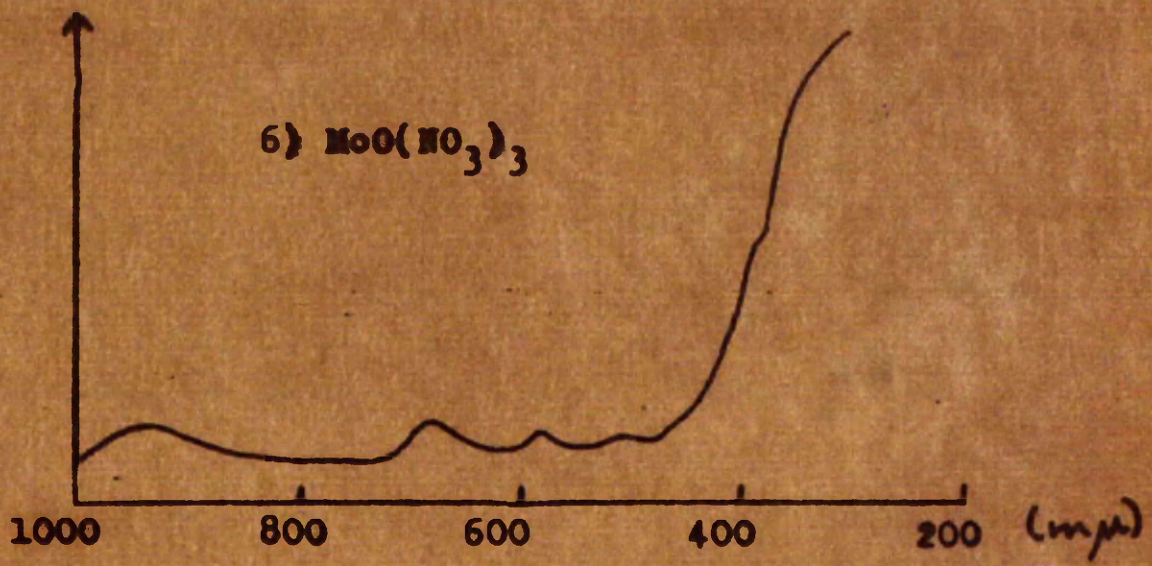

6) $MoO(NO_3)_3$
1000
800
600
400
200
(mμ)

TABLE 1.

REFLECTANCE SPECTRUM OF THE $Cr_2Cl_9^{3-}$ ANION

$(NO)_3Cr_2Cl_9$ (mμ)	$[(C_2H_5)_4N]_3Cr_2Cl_9$ (mμ)	$CrCl_3$ (mμ)	+ Assignments (Jorgensen 1962)
950)	930 m	760 sh	$^2T_1, {}^2E \rightarrow {}^4A_2$
920) m	720 s	730	$^4T_2 \rightarrow {}^4A_2$
885)	490 s	529	$^4T_1 \rightarrow {}^4A_2$
665)			
695) s			
730)			
540 sh			
420 s			

TABLE 2

REFLECTANCE SPECTRUM OF $Cr(NO_3)_3.2N_2O_4$.

$Cr(NO_3)_3.2N_2O_4$ (mμ)	$[Cr(oxalate)_3]^{3-}$ (mμ)	+ ASSIGNMENTS (Jorgensen 1962)
900 broad	696.	$^2T_1, {}^2E \rightarrow {}^4A_2$
680 Sh	571.	$^4T_2 \rightarrow {}^4A_2$
610 s	418.	$^4T_1 \rightarrow {}^4A_2$
540 m		
460 m, broad		
400 m.		
320 s.		

TABLE 3

REFLECTANCE SPECTRUM OF THE $[Mo_3Cl_{10}]^{3-}$ ANION

$(NO)_3\ Mo_3Cl_{10}$		$MoCl_6^{3-}$ (Jorgensen, 1957, 1962)	
(mμ)		(mμ)	
870	m	1036	$^2T_2, {}^2E \longrightarrow {}^4A_2$
750	m	676	$^4T_2 \longrightarrow {}^4A_2$
680	s	506	
640	s	407	$^4T_1 \longrightarrow {}^4A_2$
560	s		
425	s		

TABLE 4

REFLECTANCE SPECTRUM OF $MoO(NO_3)_3$

$MoO(NO_3)_3$		$NH_4\ _2(MoOCl_5)$ (Gray & Hare 1962)
(mμ)		(mμ)
930	m	725
685	m	435
590	m	375
520	w	312
400	sh	280
		240
		211

EXPERIMENTAL

CHROMIUM

Chromic Chloride/Nitrosyl Chloride.

Nitrosyl chloride, dried by vacuum distillation over phosphorus pentoxide, was vacuum distilled into a Carius tube containing 1 - 1.5 gms anhydrous chromic chloride. The tube was sealed, and the reaction mixture allowed to rise to room temperature. No reaction occurred, even on heating, and the original materials were recovered without change.

Chromous Chloride.

Chromous Chloride, $CrCl_2$, was prepared by passing hydrogen chloride gas, dried by bubbling through concentrated sulphuric acid, over metallic chromium at 900 - 1000°. The reaction was carried out in a silica tube. The chromous chloride sublimed from the reaction tube and was condensed in a receiver at room temperature. On completion of reaction, the system was flushed with dry nitrogen, and the receiver containing chromous chloride sealed and transferred to the dry-box.

Analysis Cr : 42.3 Cl : 57.6

$CrCl_2$ required Cr : 42.3 Cl : 57.7

Chromous Chloride/Nitrosyl Chloride.

Nitrosyl chloride was dried by distillation over phosphorus pentoxide and then vacuum distilled into a Carius tube containing chromous chloride. The tube was sealed and the reaction mixture raised to room temperature. Reaction was rapid at this temperature and a yellow-brown solid separated out. When the excess solvent was removed in vacuo, a yellow-brown residue remained. This was transferred to the dry-box for further handling.

Analysis:	N = 7.9	Cr : 20.0	Cl : 61.9
$(NO)_3Cr_2Cl_9$ requires	N = 8.2	Cr : 20.2	Cl : 62.2

Chromous Chloride/Chromic Chloride/Nitrosyl Chloride.

A mixture of chromic chloride (c 1.5 gms) and chromous chloride (c 0.05 gms) was made up in the dry-box and transferred to a Carius tube, and then evacuated. Dry nitrosyl chloride was vacuum distilled onto the mixture, the tube sealed, and the reaction allowed to come up to room temperature. Reaction was very rapid, and a yellow-brown solid precipitated out. On removal of excess solvent, a yellow-brown solid remained.

Analysis:	N: 8.3	Cr: 20.0	Cl : 62.0
$(NO)_3Cr_2Cl_9$ requires	N: 8.2	Cr: 20.2	Cl : 62.2

Chromic Chloride/Dinitrogen Tetroxide.

Dry dinitrogen tetroxide was vacuum distilled into a Carius tube containing anhydrous chromic chloride. The tube was sealed and the mixture allowed to rise to room temperature. No reaction occurred. The mixture was heated up to 100°C, but no reaction occurred.

This procedure was repeated, distilling dry acetonitrile into the Carius tube, as well as dinitrogen tetroxide. No reaction occurred in this instance or when nitromethane was used.

Chromous Chloride/Dinitrogen Tetroxide

Dry dinitrogen tetroxide was vacuum distilled into a Carius tube containing chromous chloride. The tube was sealed, and when the mixture rose to room temperature, rapid reaction occurred, a green solid being precipitated out of solution. The excess solvent was removed by vacuum distillation, and the green solid transferred to the dry-box for further examination.

Analysis. Cr: 11.8% Total N: 21.2% NO_3^-:67.8%

$Cr(NO_3)_3.2N_2O_4$ requires Cr: 11.7% Total N: 21.7% NO_3^-:68.7%

Chromic Chloride/Chromous Chloride/Dinitrogen Tetroxide.

A mixture of chromic chloride (c.1.5 gms) and chromous chloride (c.0.1 gms) was made up in the dry-box,

and transferred to a Carius tube, then transferred to the vacuum line. Dry dinitrogen tetroxide was distilled into the Carius tube, and the tube sealed. On raising the mixture to room temperature. Slow reaction occurred, while at 40°-50°C the rate increased; at room temperature, complete reaction required 3 - 4 hours in a 'shaker'.

Analysis Cr : 11.3% Total N : 21.9% NO_3^-: 68.0%

$Cr(NO_3)_3.2N_2O_4$ requires Cr:11.7% Total N: 21.7% NO_3^-:68.7%

Chromium Trioxide/Nitrosyl Chloride.

Dry nitrosyl chloride was vacuum distilled into a small reaction flask (c.50 mls) containing 1.5 - 2.0 gms chromium trioxide CrO_3. Dry air was admitted to the reaction mixture, and the flask removed from the vacuum system. It was allowed to warm up under atmospheric pressure with a calcium chloride guard tube. At about 0°C, fairly vigorous reaction took place, and a black solid was formed. Removal of excess solvent and the volatile reaction products left a very shiny black crystalline solid, which was transferred to the dry box for further handling.

Chromate was analysed by precipitation as barium chromate; total chromium was analysed for by oxidation of the chromium (III) to chromium (VI) with sodium peroxide Na_2O_2, and precipitation of this, plus the original chromate,

as barium chromate.

Analysis : Found

N : 7.2% Cr(VI) ; 27.1% Total Cr : 41.1% Cl : 9.5%

$(NO)_2 . Cr_3O_8Cl$ requires

N : 7.4% Cr(VI) : 27.5% Total Cr : 41.2% Cl : 9.4%

Chromium Trioxide/Dinitrogen Tetroxide.

Dry dinitrogen tetroxide was vacuum distilled into a Carius tube containing chromium trioxide. The tube was sealed, and the reaction raised to room temperature. The dinitrogen tetroxide turned fairly bright green, but the chromium trioxide appeared to be only very slightly soluble.

Gas phase infrared analysis of the dinitrogen tetroxide gave no indication of chromyl linkages being present, and complete removal of the solvent in vacuo left only a residue of chromium trioxide.

Chromyl Chloride.

Chromyl chloride was prepared by a method analogous to the preparation of vanadium oxytrichloride (previous chapter - experimental section).

Anhydrous aluminium trichloride was sublimed to purify it and remove traces of moisture. A solid mixture of anhydrous $AlCl_3$ and 40 - 50% excess of chromium trioxide,

according to the equation below, was made up.

$$3CrO_3 + 2AlCl_3 \longrightarrow 3CrO_2Cl_2 + Al_2O_3$$

This mixture was ground up intimately in the dry-box, transferred to a 100 mls reaction flask, then evacuated. Even at room temperature, chromyl chloride distilled slowly out of this mixture, and the rate became quite rapid at 70° - 80°C. The chromyl chloride was condensed in a trap containing phosphorus pentoxide, and redistilled in vacuo to dry it thoroughly.

Analysis Found Cr(as chromate) : 33.5% Cl: 45.4%

CrO_2Cl_2 requires Cr : 33.6% Cl : 45.8%

Chromyl Chloride/Nitrosyl Chloride

Chromyl chloride, prepared as previously explained, was vacuum distilled into a 50 ml. reaction flask; dry nitrosyl chloride was vacuum distilled separately into the same flask. Dry air was admitted, and the reaction allowed to rise to room temperature protected from moisture with a calcium chloride guard tube. No vigorous reaction occurred but around 0°C a small quantity of solid separated out. Gas phase infrared examination of the volatile residue indicated only excess of NOCl present. The volatile residue was removed in vacuo and the green

solid residue examined. There was insufficient for analysis, but infrared data were obtained.

Chromyl Chloride/Dinitrogen Tetroxide.

Chromyl chloride and dinitrogen tetroxide were separately distilled in vacuo into the same reaction flask, dry air admitted, and the mixture allowed to rise to room temperature protected from moisture with a calcium chloride guard tube. After completion of reaction, a small solid residue was observed. Infrared examination of the volatile residue indicated that a mixture of dinitrogen tetroxide and nitrosyl chloride was present but no evidence was observed for chromyl groups or co-ordinated nitrato-groups.

After removal of the volatile residue, a blue-green solid remained. Insufficient was recovered for analysis, but infrared data were obtained.

Chromium/Dinitrogen Tetroxide/Acetonitrile.

Dinitrogen tetroxide was vacuum distilled into a Carius tube containing metallic chromium, and acetonitrile separately distilled into the same tube. The tube was then sealed, and the mixture raised to room temperature. No reaction was observed. On heating to 80°C for 2 - 3 hours no reaction could be initiated;

neither could shaking at room temperature for 2 - 3 weeks. initiate a reaction.

Molybdenum Trichloride/Nitrosyl Chloride.

Nitrosyl chloride was vacuum-distilled in about 3 : 1 stoicheiometric excess into a Carius tube containing molybdenum trichloride. The tube was sealed and the reaction allowed to rise to room temperature, when steady reaction occurred. The reaction was left for 24 hours.

The tube was opened and excess solvent removed in vacuo, maintaining the reaction mixture at -20°C (carbon tetrachloride slush bath) to avoid loss of the volatile reaction product. When all the excess nitrosyl chloride had been removed, the solid residue was transferred rapidly, in a dry-box, into a sublimer. The volatile fraction sublimed out at 90°- 93°C, as a very deep blue-purple solid.

Analysis	N : 5.5%	Mo : 39.1%	Cl : 48.7%
$(NO)_3 Mo_3 Cl_{10}$ required	N : 5.7%	Mo : 39.3%	Cl : 48.4%

The pale brown product was involatile up to 200°C.

Analysis	Mo : 40.0%	Cl : 59.5%
$MoCl_4$ requires	Mo : 40.3%	Cl : 59.7%

Molybdenum Trichloride/Dinitrogen Tetroxide.

Dinitrogen tetroxide was vacuum distilled into a Carius tube containing molybdenum trichloride, and the tube sealed. The mixture was raised to room temperature

and a steady reaction was observed to occur, which came to completion in 3 - 4 hours. On removal of excess solvent a very pale green solid remained, which was transferred to the dry-box for further handling.

Analysis	Mo : 31.5%	NO_3^- : 61.6%
$MoO(NO_3)_3$ requires	Mo : 31.9%	NO_3^- : 61.9%

Molybdenum Pentachloride.

A stream of chlorine, from a cylinder, was dried by bubbling through concentrated sulphuric acid, then passed over molybdenum metal heated to 200° - 250° in a long reaction tube. The molybdenum pentachloride was formed immediately and sublimed off the reaction surface, condensing on the cooler parts of the tube. On completion of reaction the tube was swept out with nitrogen, then transferred to the dry-box.

Analysis	Mo : 35.15%	Cl : 64.82%
$MoCl_5$ requires	Mo : 35.10%	Cl : 64.90%

Molybdenum Pentachloride/Nitrosyl Chloride.

Nitrosyl chloride was vacuum distilled into a Carius tube containing molybdenum pentachloride, prepared as above. The tube was sealed and the mixture raised to room temperature, when reaction was observed to occur. The excess solvent was removed in vacuo, and the pale grey

solid residue examined.

Analysis	N : 3.8%	Mo : 27.8%	Cl : 62.1%
$NO.MoCl_6$ requires	N : 4.1%	Mo : 28.3%	Cl : 62.8%

Infrared spectra were measured on a Grubb-Parsons DB1 spectrophotometer in Nujol mulls. The free nitrosonium ion bonds of $(NO)_3Cr_2Cl_9$ and $(NO)_3Mo_3Cl_{10}$ were calibrated in florube mulls against polystyrene film. Since the structure of $Cr(NO_3)_3.2N_2O_4$ was not definitely ascertained, the 2336 cm^{-1} and 2278 cm^{-1} bonds were not calibrated.

All reflectance spectra were measured, diluted in potassium chloride, on a Hilger Watts Uvispek Spectrophotometer Model H700 307; the dry-box was invariably used for making up the reflectance samples.

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A B S T R A C T

A series of compounds, reported in the literature, which can be formulated as nitrosonium salts of fluoro-acids, have been re-prepared. Several metal chloride-nitrosyl chloride adducts, also reported in the literature, have been re-prepared, and both these groups of compounds have been shown to contain the nitrosonium ion, NO^+, by infrared diagnostic methods.

The isomorphism of the nitrosonium salts of the anions fluoroborate, chlorostannate and chloroplatinate with their potassium analogues has been confirmed, and nitrosonium and potassium fluorosulphates have been shown to be isostructural. These observations have been explained structurally, with reference to the relative sizes of nitrosonium and halide ions.

The free (i.e. unco-ordinated) nitrosonium ion was found to absorb in the region 2160 cm^{-1} - 2400 cm^{-1}. This wide variation was partially explicable in terms of polarisation by the anion but it is apparent that other factors were important. In general, it was found that fluoro-acid salts gave the highest nitrosonium ion stretching frequencies, followed by oxy-acid salts and chloro-acid salts respectively.

The behaviour of group IVB and VB Lewis acid halides was observed with nitrogen oxides and nitrosyl chloride. With dinitrogen tetroxide, all the compounds examined, except arsenic trichloride, gave a mixture of products which it was not possible to separate. Arsenic trichloride gave a nitrosonium nitrato-arsenate salt. In the other cases, there was evidence for the formation of nitrosonium and nitronium salt mixtures, in accord with earlier observations on the behaviour of dinitrogen tetroxide with Lewis acids, and strong acids such as perchloric acid. With nitrosyl chloride, the products were either nitrosonium chloro-acid salts or molecular adducts. Reactions involving nitric oxide were not investigated extensively but in reactions with high valency metal chlorides, the primary reaction steps was always a reduction by the nitric oxide.

The behaviour of transition metal chlorides and oxides of the titanium, vanadium and chromium groups was observed in nitrosyl chloride and dinitrogen tetroxide. These reactions could all be explained assuming auto-ionisation of the solvent.

The reactions in nitrosyl chloride yielded mainly nitrosonium salts of chloro-acids, and several of the anions thus formed were bi- and tri- nuclear species.

The previously reported compounds $NO.VCl_4$ and $NO.V_2Cl_7$ were obtained and characterised as nitrosonium salts. With niobium and tantalum, the new compounds $NO.NbCl_6$ and $NO.TaCl_6$ were prepared, containing the previously unknown $NbCl_6^-$ and $TaCl_6^-$ anions. The new compounds $(NO)_3\ Cr_2\ Cl_9$ and $(NO)_3\ Mo_3\ Cl_{10}$ were obtained. A surprising feature of several of these ionic compounds was their high volatility.

In the reaction between chromium (VI) trioxide and nitrosyl chloride, a new compound $(NO)_2\ Cr_3\ O_8\ Cl$ was characterised, in which chromium has undergone a partial reduction. Vanadium pentoxide underwent a similar reaction, but in this case it was not reproducible.

The reactions involving dinitrogen tetroxide generally gave rise to one product only, in contrast to the Lewis acid - dinitrogen tetroxide reactions. The products were usually metal nitrate-dinitrogen tetroxide adducts and these could be formulated as nitrosonium metal nitrato-salts, on the basis of their infrared spectra. Vanadium and chromium chlorides gave the adducts $VO_2NO_3.N_2O_4$ and $Cr(NO_3)_3.2N_2O_4$ respectively, but molybdenum trichloride gave $Mo(V)O(NO_3)_3$, which may be polymeric.

No reaction occurred between chromium (III) chloride and either nitrosyl chloride or dinitrogen tetroxide, but in the presence of chromous chloride, reaction proceeded

readily in both instances.

No reaction was observed between high valency metal oxides and dinitrogen tetroxide, but this may have been due to insufficiently vigorous conditions.

The reflectance spectra of the majority of the above compounds were observed, and, in most cases it was possible to make satisfactory band assignments.